การเลือกเกิดปฏิกิริยาไฮโดรจีเนชันของ 2-เฮกซีนแนล เป็น 2-เฮกซีนอล บนตัวเร่งปฏิกิริยาฐานโคบอลต์

SELECTIVE HYDROGENATION OF 2-HEXENAL TO 2-HEXENOL OVER COBALT-BASED CATALYSTS

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โครงงานพิเศษนี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรวิทยาศาสตรบัณฑิต

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A SPECIAL PROJECT SUBMITTED IN PARTIAL FULFILLMENT

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Year	2013		
Advisor	Assoc. Prof. Dr. Tawan Sooknoi		
Co-Advisor	Dr. Natthida Numwong		

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ABSTRACT

Selective hydrogenation of 2-hexenal to 2-hexenol was carried out in continuous fixed bed down-flow reactor at 80 °C using metal-cobalt supported silica (M-Co/SiO_2, M= Cu, Fe and Pt) catalysts prepared by impregnation method. The calcined Co/SiO_2 catalyst shows Co_3O_4 phase on amorphous silica. After platinum, copper, and iron were incorporated, the similar surface areas with high metal dispersion were obtained. Upon reduction, the CoPt and CoCu alloys were formed. Some of CoFe alloy was found together with CoFe mixed oxide and iron oxide. CO_2-TPD shows that the basicity of Co/SiO_2 catalyst is higher than that of CoCu/SiO_2 catalyst. 2-hexenal can be hydrogenated to 2-hexenol and hexanal follow by hydrogenation to hexanol. Moreover, hexanal can be converted to high molecular weight aldol compound. CoPt/SiO_2 catalyst is selective for hydrogenation at carbonyl group as compared to other cobalt-based catalysts. CoFe/SiO_2 and CoCu/SiO_2 catalysts show low activity for hydrogenation but promote undesirable aldol products. Using methanol as a solvent facilitated isomerization of the 2-hexenal and prevents aldol condensation.

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Selective hydrogenation of reactant with unsaturated functional groups is important for the production of various chemicals. For example, unsaturated alcohols obtained from selective C=O hydrogenation of α,β-unsaturated aldehydes are useful in the production of perfumes, flavors, fragrance, and pharmaceuticals [1]. However, in typical hydrogenation catalysts, the hydrogenation of the C=C group is more favorable than that of the C=O group [2-5], which predominantly promote undesirable saturated aldehydes or alcohols with low selectivity towards desirable unsaturated alcohol products [4, 5]. (The pathway for the hydrogenation of α,β-unsaturated aldehydes is shown in Figure 1.1)

Accordingly, it is interesting to search for a catalyst that interact strongly with the C=O group in order to improve the selectivity to more desirable unsaturated alcohol. This can be achieved by incorporation of oxophilic metal with noble metal [5]. Because of oxophilic metals such as Co and Fe are strongly adsorbed the carbonyl group and show lower hydrogenation activity. Thus the hydrogenation activity of noble metals such as Pt and Cu can be optimized [6, 7]. Therefore, the incorporated oxophilic metal with noble metal is interested to be used as a catalyst for selective hydrogenation.

Consequently, in this thesis, CoCu, CoPt, and CoFe supported on SiO_2 prepared by wetness impregnation method were used as catalysts for the hydrogenation of 2-hexenal. Effect of reaction temperature, contact time, type of metal loaded, and solvent were studied and the selective hydrogenation of unsaturated aldehydes was investigated over these catalysts.

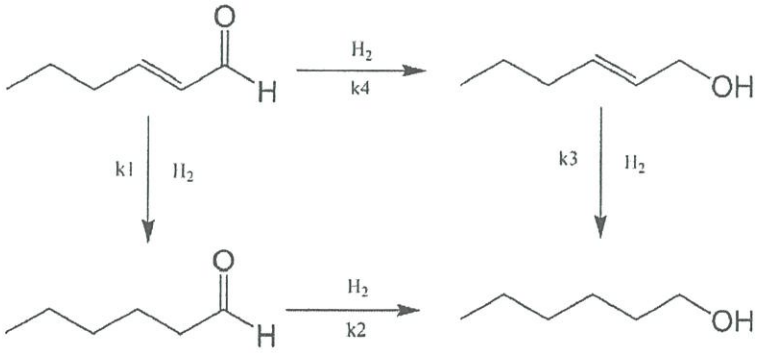


Figure 1.1: Reaction pathway of the hydrogenation of α,β- unsaturated aldehydes.

1.2 Objectives

The specific objectives of this thesis are as follows:

1.2.1 To investigate the production of 2-hexenol from selective hydrogenation of 2-hexenal.

1.2.2 To understand the role of catalyst in selective hydrogenation activity and selectivity.

1.2.3 To understand effect of different metal loaded on cobalt-based catalyst.

1.2.4 To obtain appropriate reaction conditions for hydrogenation with reasonable catalyst stability.

1.3 Scopes of the study

The scopes of this thesis are as follows:

1.3.1 Synthesis and modification

1.3.1.1 Synthesize different metal-cobalt supported silica (M-Co/SiO_2) catalysts by wetness impregnation method.

1.3.2 Characterization of the catalysts

1.3.2.1 Investigate the physical properties of the catalysts using conventional techniques, such as X-ray powder diffraction (XRD).

1.3.2.2 Investigate the temperature reduction of metal-cobalt catalyst by temperature programmed reduction (TPR).

1.3.2.3 Investigate surface area and porosity of the catalysts by gas adsorption analysis (BET).

1.3.2.4 Investigate basicity of the catalysts by CO_2-temperature program desorption (CO_2-TPD)

1.4 Catalytic testing

1.4.1 Investigate catalytic activity and selectivity of modified catalysts for the selective hydrogenation of 2-hexenal in a continuous fixed bed down-flow reactor.

1.4.2 Study the effect of different metal loaded on cobalt-based catalysts on the activity and selectivity for the selective hydrogenation of 2-hexenal.

1.4.3 Study the effect of reaction condition: reaction temperature, contact time, and solvent on the selective hydrogenation of 2-hexenal.

1.4.4 Study on stability of catalysts.

1.5 Analysis and quantification of products

Determine the amount of products online by Gas chromatography with flame ionization detector (GC-FID).

1.6 Expected and results

It is expected that a new technology for production of 2-hexenol from hydrogenation of 2-hexenal under atmospheric pressure will be obtained.

CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Unsaturated alcohol

Unsaturated alcohols such as nerol and geraniol are important compounds as intermediates for the production of organic compounds useful as synthetic resins, drugs, flavors, and the like. The unsaturated alcohol is produced by hydrogenating a corresponding unsaturated carbonyl compound in the presence of a hydrogenation catalyst [8].

Reactant structure can affect the maximum selectivities for desired products obtained over heterogeneous catalysts. The branching in the vicinity of ethylenic double bond favors high selectivities for unsaturated alcohols, which means that the selectivities for unsaturated alcohols decrease in the following reactants: cinnamaldehyde > 3-methylcrotonaldehyde > crotonaldehyde > acrolein [9]. There are several reasons, which might affect the product selectivity with different substrates, like electronic and inductive effects in the reactant, adsorption mode of the reactant and the geometrical restrictions of the metal surface.

In the past, effort to produce unsaturated alcohols by the catalytic hydrogenation of the corresponding alpha, beta-olefinically unsaturated aldehydes have in general low successful [10].

Therefore, the present invention solves the problems of the conventional art as described above, and intends to provide a hydrogenation catalyst for a carbonyl group, which is capable of economically producing an unsaturated alcohol by hydrogenating an unsaturated carbonyl compound with high selectivity with a simple process and a method of efficiently producing the hydrogenation catalyst. Further, the present invention intends to provide a practical method of producing an unsaturated alcohol using the hydrogenation catalyst [8].

Table 2.1 Information of reactant properties

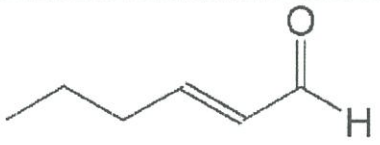
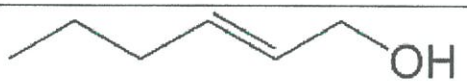
Reactant	
Chemical Name	2-hexenal
Molecular Formula	$C_6H_{10}O$
Formula Weight	98.14
Boiling Point	146.50°C
Flash Point	38.33°C
Density	0.846 g/mL at 25°C (lit.)
Vapor density	3.4 (vs air)
Vapor pressure	10 mm Hg (20°C)
Solubility	Insoluble in water; soluble in alcohol
Application	Odor Description: A green, citrusy, orange, pungent odor
Flavor Use	Many uses including green fruit, kiwi, peach, green apple, berry, strawberry, fresh blueberry, cherry, tea, orange, citrus and raspberry.

Table 2.2 Information of product properties

Product	
Chemical Name	2-hexenol
Molecular formula	$C_6H_{12}O$
Molecular weight	100.16 g/mol
Density	0.84 g/cm^3
Flash Point	56°C
Boiling Point	156-160°C

2-hexenol is an aliphatic alcohol group and isomer is cis-2-hexenol. It is colorless liquid which is slightly soluble in water. 2-hexenol is able to prepared by the hydrogenation of 2-hexenal. It is used as a fragrance in cosmetics and food industries.

2.2 Hydrogenation

Hydrogenation is a chemical reaction between molecular hydrogen (H_2) and another compound or element, usually in the presence of a catalyst. The process is commonly employed to reduce or saturate organic compounds.

Hydrogenation typically constitutes the addition of pairs of hydrogen atoms to a molecule. Catalysts are required for the reaction to be usable; non-catalytic hydrogenation takes place only at very high temperatures. Hydrogenation reduces double and triple bonds in hydrocarbons [11].

$$RCH{=}CH_2 + H_2 \longrightarrow RCH_2CH_3 \ (R = \underline{\text{alkyl}}, \underline{\text{aryl}})$$

Below is a rough reactivity order of functional groups towards catalytic hydrogenation. Note that the details of substrate structure as well as the metal used, and solvents can alter this sequence in specific cases [12].

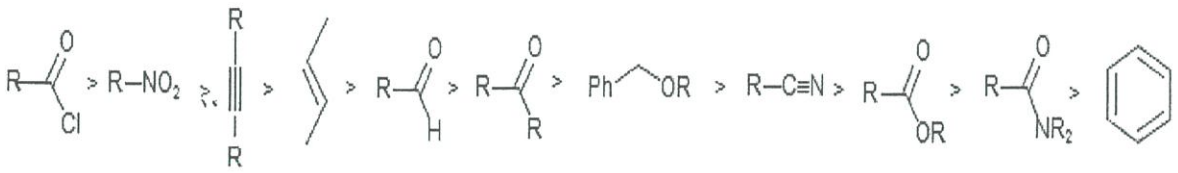


Table 2.3 Important characteristic of typical substrates [11].

substrate	Product	Comments
alkene, $R_2C{=}CR'_2$	alkane, $R_2CHCHR'_2$	many catalysts, major application is margarine

alkyne, RCCR	alkene, cis-RHC=CHR'	over-hydrogenation to alkane can be problematic
aldehyde, RCHO	primary alcohol, RCH_2OH	easy substrate
Unsaturated aldehyde, RC=CCHO	Unsaturated alcohol, $RC=CCH_2OH$	challenging substrate
ketone, R_2CO	secondary alcohol, R_2CHOH	more challenging than RCHO, prochiral for unsymmetrical ketones
ester, RCO_2R'	two alcohols, RCH_2OH + R'OH	challenging substrate
imine, RR'CNR"	amine, RR'CHNHR"	easy substrate, often use transfer hydrogenation, actual precursor is N-protonated
amide, $RC(O)NR'_2$	amine, $RCH_2NR'_2$	challenging substrate
nitrile, RCN	primary amine, RCH_2NH_2	product amine reactive toward precursor nitrile in some cases
nitro, RNO_2	amine, RNH_2	commercial applications use heterogeneous Ni and Ru catalysts; major application is aniline

2.2.1 Hydrogenation of Aldehydes

Aldehydes are usually easily hydrogenated to the corresponding alcohols over most of the transition metal catalysts. The rate of hydrogenation of carbonyl compounds, however, depend on the nature of catalysts; the structure of compounds; the reaction medium; as well as the reaction condition; additives or the impurities associated with catalyst preparation greatly influence the rates of hydrogenation and in some cases the product selectivity [13].

2.2.2 Hydrogenation of unsaturated aldehydes

Usually, unsaturated aldehydes in which C=C bonds are not conjugated with the C=O bonds are preferentially hydrogenated to saturated aldehydes and saturated alcohols unless the C=C bonds are highly hindered [13].

α,β-unsaturated aldehydes may be hydrogenated to the corresponding unsaturated alcohols by selecting appropriate catalysts and reaction conditions. The unsaturated alcohols depend on various factors such as the structure of aldehyde, the nature of catalyst, and the presence of additive, as well as other reaction conditions. The selectivity in the hydrogenation of α,β-unsaturated aldehydes, therefore, has been a subject of many investigations using various catalysts or catalysts systems [13].

Hydrogenation of α,β-unsaturated aldehydes is a challenge of high importance as hydrogenation of the C=C bond leads to saturated aldehyde used in the flavouring industry and in the synthesis of pharmaceuticals, while hydrogenation of the C=O bond produces unsaturated alcohol is important for the chemical industry for example used in the manufacture of perfumes.

2.3 Chemo-selective hydrogenation

The selective hydrogenation of the α,β-unsaturated aldehydes is well-documented reaction with important applications in the industrial field. It gives three types of products, following the C=C bond is hydrogenated giving a saturated aldehyde or the C=O bond is involved yielding an unsaturated alcohol; finally, a total hydrogenation can occur and a saturated alcohol is obtained. The most important product, from an industrial view point is the unsaturated alcohol. This compound is also the most difficult to obtained because the hydrogenation of the C=C bond is thermodynamically and kinetically favoured over the C=O bond [14]. A considerable attention has been focused on heterogeneous hydrogenation by metal, which have strong affinity for the C=O bond [3], The promoter effect of metal is attributed to ionized metal species, which acting

as a Lewis acid, interacts with the oxygen atom of the carbonyl bond (basic group), thus weakening the C=O bond and favouring its hydrogenation. Furthermore lowering the number of sites that strongly interact with hydrogen and chemisorb the α,β- unsaturated aldehydes through the olefinic bond can hinder the C=C hydrogenation reaction rate [4], with the aim to remain both activity and selectivity towards the unsaturated alcohol [15].

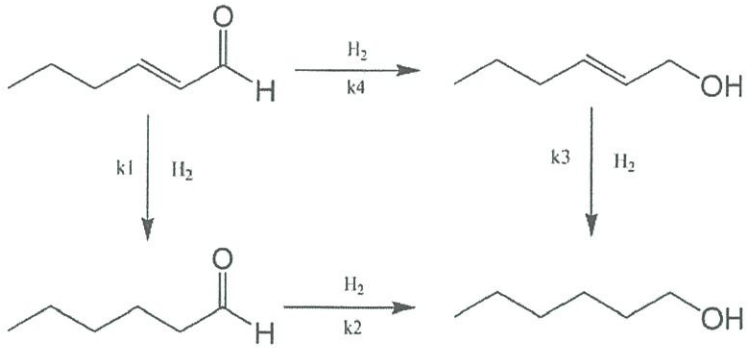


Figure 2.1: Reaction pathway of the hydrogenation of α,β- unsaturated aldehydes

Hydrogenation has three components, the unsaturated substrate, the hydrogen (or hydrogen source) and a catalyst. Hydrogenation itself is not reactive towards organic molecules, all useful reactions involve transition metal catalysts. The most used ones for hydrogenation reaction are noble metal such as Pd, Pt, Rh, Ni, and Ru [16]. The reduction reaction is carried out at different temperatures and pressures depending upon the substrate and the activity of the catalyst [11].

2.4 Heterogeneous catalysts

The chemo-selective hydrogenation of a carbonyl bond in multi-unsaturated aldehydes to unsaturated alcohol is a difficult task, since the thermodynamics favors of C=C hydrogenation over C=O. These unsaturated alcohols are used as fragrances and drugs, which are industrial interest. In principle these compounds can be selectively hydrogenated by using homogeneous catalysts, but the heterogeneous catalysts are more environmental friendly, easier to separate and re-use than their homogeneous counterparts [9].

Heterogeneous catalysts for hydrogenation are common industrially. The activity is adjusted through changes in the environment around the metal. Heterogeneous catalysts are

affected by their supports [11]. Catalysts with rare exceptions, no reaction below 480°C (477°C or 482°C) occurs between H_2 and organic compounds in the absence of metal catalysts. The catalyst binds both the H_2 and the unsaturated substrate and facilitates their union. Platinum, palladium, rhodium, and ruthenium form highly active catalysts, which operate at lower temperatures and lower pressures of H_2. Non-precious metal catalysts, especially those based on nickel (such as Raney nickel and Urushibara nickel) have also been developed as economical alternatives, but they are often slower or require higher temperatures. The trade-off is activity (speed of reaction) vs. cost of the catalyst and cost of the apparatus required for use of high pressures. Notice that the Raney-nickel catalysed hydrogenations require high pressures [11].

2.4.1 Noble metals

The noble metals are most commonly considered to be ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, and gold. Other sources include mercury, rhenium or copper as a noble metal. On the other hand, titanium, niobium, and tantalum are not included as noble metals [6].

Noble metal catalysts have been considered as viable alternatives to the present industrial catalyst. The type of dispersed metal on the solid support has an influence on hydrogenation. Many reports noted about how is noble metal has an important influence on the hydrogenated carbonyl compound. Many studies have shown that these metals are much more active. Throughout the literature the most commonly reported active catalysts are the noble metals, platinum (Pt) and palladium (Pd). All reported the activity of hydrogenation catalyst is: Pt < Rh < Ir < Ni < Pd < Cu [7].

However, the hydrogenation of the C=C group is more favorable than that of the C=O group. Therefore, the hydrogenation of α,β-unsaturated aldehydes towards saturated aldehydes or saturated alcohol, which are undesirable products [17], is predominantly promoted over typical hydrogenation catalyst. In contrast, the selectivity of unsaturated alcohol is generally low, thus catalysts must interact strongly with the C=O group in order to improve the selectivity to the more desirable unsaturated alcohol. This can be achieved by incorporation of noble metal with oxophilic metal. Because of oxophilic metals such as Co and Fe are strongly adsorbed the carbonyl group. Therefore, the incorporated oxophilic metal with noble metal is interested to be used as a catalyst for selective hydrogenation.

2.4.2 Metal selection

The adsorption phenomenon is limited by many factors, e.g. by the mode of reactant adsorption on a specific metal surface. However, the electronic structure of the metal can be changed by adding a second metal, leading for instance to alloy formation, by changing the metal particle size or by enhancing interactions with the support. The selection of metal used in chemo-selective hydrogenation of unsaturated compounds is important by taking into account the structure of the metal, i.e. where group in the periodic table it is located. Additionally, the metal dispersion, the catalyst pretreatment as well as the effect of support and additives are needed to be considered with the main aim to correlate the catalyst structure with activity and selectivity. As it will be seen a rational catalyst design for chemoselective hydrogenation yielding predefined selectivities and an activity is a very demanding task [9].

2.4.3 Monometallic catalysts

In the conventional monometallic catalysts, the metals are selected from group 10, e.g. Ni, Pd and Pt. In addition, Rh from group 9 and Ru from group 8 also have been used as catalysts. The supports are usually alumina, silica and carbon. The catalytic activity of different metal supported catalysts in hydrogenation is determined by ability to activate C=C and C=O bonds as well as the activity of hydrogen to react on the metal surface. Hydrogen activity on different metals is relatively well understood on the basis of adsorption studies and fundamental theories [9]. The hydrogenation activities and selectivities are presented for different groups in the periodic table by starting from group 8. Note that the selectivities to the desired products over metal supported catalysts depend not only on the metal, but also on the reactant structure.

The group 8 metals: Ru and Os, which are electropositive have used in chemoselective hydrogenation. Os has been used in very few papers as a catalytic metal supported on SiO_2, and on TiO_2. In the hydrogenation of oxopromegestone, Os was the most selective among tested metals, but the catalytic activity was low. However, the hydrogenation rate over Ru catalyst was quite low with relatively low selectivities.

Monometallic catalysts containing a metal from group 9 (Co, Rh, and Ir) have been used in several chemoselective hydrogenations. The Monometallic group 9 metal catalysts can act quite selectively in some cases. In general, it can be stated that Co being not a noble metal, is more selective to unsaturated alcohols than Rh, Ru or Pt. The selectivity to unsaturated alcohols can be tuned by changing the surface structure of Co, which exists in four different forms.

Chemoselective hydrogenation over group 10 metals: Ni, Pd, Pt was also investigated. Platinum has been the most intensively used as the active metal in chemoselective hydrogenations. Pt is not intrinsically selective to produce unsaturated alcohols, although high selectivities to unsaturated alcohols could be still achieved depending very much on the sterical structure of the reactant. Pd differs from the other metals in group 10 from the selectivity point of view, as it is very selective to hydrogenate ethylenic bond. Ni supported catalysts are very selective in some chemoselective hydrogenations.

On the other hand, group 11 metals: Cu, Ag, Au catalysts are usually less active for chemoselective hydrogenation than metal from the other groups.

2.4.4 Bi- and multimetallic catalysts

Bimetallic catalysts have been very selective in several chemoselective hydrogenations. The origin for the high selectivities to unsaturated alcohols has been associated with electron transfer from the less noble metal to more noble metal as well as alloy formation and/or an intimate contact between two metals. The second metal can exist in alloy, in ionic state as well as in partially oxidized form. The difference in the electronegativity between two metals can enable the polarization of the carbonyl bond. Additionally, geometrical effects, like a change in metal dispersion, decoration of the main metal by the second metal via surface enrichment. It is important to note that these effects are often coexistent in bimetallic catalysts and thus one effect, like for instance alloy formation in a model catalyst. Alloys are defined as compounds formed by two or more metals; they can also be formed between a metal and another metal originating from a non-inert support. The alloy formation is strongly influenced by the selection of metal precursor and support, catalyst pretreatment as well as the preparation method. In order to uncover both the selective hydrogenation site and the reaction, mechanism it is important to know the chemical nature of the active site [9].

In general, it can be concluded that the bimetallic supported catalysts can be more active and selective in chemoselective hydrogenations than the corresponding monometallic catalysts. The reason for this positive behavior is the formation of interfacial metal-support sites and/or alloys.

For example, the hydrogenations of unsaturated aldehydes are an important model reaction. In the presence of heterogeneous catalysts both the aldehyde and the olefinic double bond of unsaturated aldehydes can be hydrogenated [18]. It has been demonstrated that supported

platinum catalysts modified by tin, germanium, cobalt, or iron have much higher selectivities for the hydrogenation of the aldehyde group than the unmodified one [19]. With respect to the form of promoters in modified platinum catalysts the role of ionic species has been emphasized. It has also been suggested that in supported Sn-Pt catalysts the Sn^{n+}–carbonyl interaction is responsible for the increased $S_{C=O}$ selectivity [20]. This interaction, as shown in Figure 2.2, requires the formation of "Sn^{n+}–Pt ensemble" sites, i.e. ionic Sn^{n+} species stabilized either at the metal site or the metal-support interface. It should also be emphasized that in the selective hydrogenation of unsaturated aldehydes, in addition to the formation of "Sn^{n+}–Pt ensemble" sites, the adsorption of both the substrate and the formed unsaturated alcohol with their olefinic double bond should also be suppressed [17].

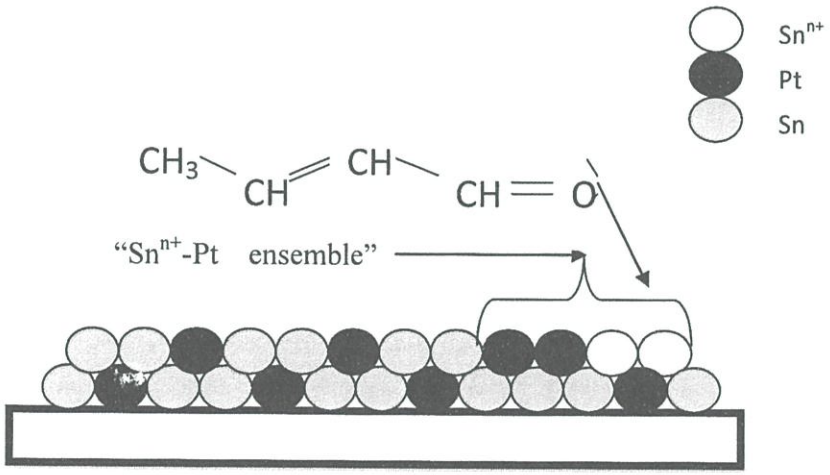


Figure 2.2: The formation of " Sn^{n+}–Pt ensemble " sites

2.4.5 Metal particle size and shape

The concept of structure-sensitivity, which applies that the hydrogenation activity and selectivity are dependent on the metal particle size or metal dispersion. Additionally, the change in metal particle size can affect the electronic and geometrical properties of metal particles. The smaller metal particles are known to be more electron deficient than larger ones. Furthermore, the number of edges and corners, which could have different activities and selectivities is increased in the smaller particles. The change in metal particles can simultaneously change other properties of the metal [9].

It was quickly noticed that the yield in unsaturated alcohol is not only a specificity of the catalyst alone but depends on the support [5]. In general, supported catalysts are very interesting materials because one metal can tune and/or modify the catalytic properties with the other

transition metal [21]. Metallic catalysts are usually supported on high surface area carriers, such as silica and alumina. Additionally, the preparation of supported metallic catalysts leads to catalysts with new characteristics, where a specific interaction between the two metals for selectivity towards unsaturated alcohols [5].

Activity and selectivity depend not only the metal type and dispersion but also on the support. The catalyst carriers should be able to disperse and stabilize the active metal. Support materials can exhibit inert, basic or acidic properties. Furthermore, non-inert carriers can form an alloy with an active metal [9].

2.5 Support

The main task for the support is to disperse the metal, because usually highly dispersed small metal particles are more active in activating organic molecules [9].

Heterogeneous transition metal catalysts for hydrogenation are usually employed in the states of metals, oxides or sulfides that are either unsupported or supported. The physical form of a catalyst suitable for a particular hydrogenation is determined primarily by the type of reactor such as, fixed-bed, fluidized-bed, or batch reactor. For industrial purposes, unsupported catalysts are seldom employed since supported catalysts have many advantages over unsupported catalysts. One exception to this is Raney-type catalysts, which are effectively employed in industrial hydrogenations in unsupported states. In general, use of a supported allows the active component to have a larger exposed surface area such as alumina, silica, titania, niobia, and zirconia [22], which is particularly important in those cases where a high temperature is required to activate the active component.

Unsupported catalysts have been widely employed in laboratory use. The effect of an additive or impurity appears to be more sensitive for unsupported than for supported catalysts. This is also in line with the observations that supported catalysts are usually more resistant to poisons than are unsupported catalysts [13].

2.5.1 Silica support

The study of metal particles on oxide supports is of importance in heterogeneous catalysis because the size and nature of the interaction of a metal particle with an oxide support are critical in determining catalytic activity and selectivity. It is well-known that metals on reducible oxides such as TiO_2 exhibit a strong metal–support interaction (SMSI). On the other

hand, irreducible oxides like SiO_2 are assumed to be relatively inert. However, in certain cases, silica has been shown to exhibit a metal–support interaction following a high temperature treatment. Oxidation and reduction at elevated temperatures are essential steps for the preparation of supported, high surface area catalysts; however, these treatments can cause morphological changes of the dispersed metal particles arising from sintering and/or metal–support interactions. Therefore, it is of considerable importance to investigate and define optimal conditions for catalyst preparation, pretreatment and activation. Depending on the particular metal–oxide system, various morphological changes resulting from a metal–support interaction have been reported, namely sintering and alloy formation. In particular, silicide formation from metals supported on silica has received considerable attention because of the importance of the metal–silica interface to numerous technologies. Furthermore, silicide formation between metals and SiO_2 in a catalyst has been shown to alter catalytic activity and selectivity. In spite of the numerous studies on metals supported on SiO_2 at elevated temperatures, there are still controversial and unresolved issues regarding the nature of the metal–support interaction in silica-supported catalysts [23].

Supported catalysts may be prepared by a variety of methods, depending on the nature of active components as well as the characteristics of carriers. An active component may be incorporated with a carrier in various ways, such as decomposition, impregnation, precipitation, co-precipitation, adsorption or ion exchange. Some characteristics of commonly used supporting materials are summarized in Table 2.4 [13].

Table 2.4 Characteristics of commonly used supporting materials

Carrier	Specific Surface Area (m^2/g)	Pore Volume (ml/g)	Average Pore Diameter (nm)
Activated Al_2O_3	100-350	0.4	4-9
SiO_2	300-600	0.4-0.8	2-8
Zeolite	400-900	0.08-0.2	0.3-0.8
Activated carbon	800-1200	0.2-2.0	1-4

The rational design of active and selective heterogeneous metal supported catalyst is not however very easy task. There are several factors, which can affect the activity and selectivity of

a catalyst. These are metal and support selection, metal precursor, catalyst preparation and activation methods, selection of reaction conditions and operation mode (e.g. gas or liquid phase system) [9].

In hydrogenation reaction, both vapor and liquid phase have been performed but the vapor phase hydrogenation is usually preferred because it can be carried out at normal atmospheric pressure and well-defined metal on surfaces [21]. Heterogeneous catalysts used in hydrogenation reactions contain usually a metal supported on a carrier. The metal is able to adsorb hydrogen thus making hydrogenation reaction possible. The carrier is able to disperse the metal to smaller particles as compared to bulk metal enhancing the specific metal surface area [9]. Additionally, smaller metal particles partially behave as non-metals, e.g. have higher electron densities, leading to higher hydrogenation rates compared to larger particles.

Regarding the effect of other parameters, like substrate structure, catalyst type and structure as well as solvent etc, on product selectivity, these parameters are interdependent [9].

2.6 Literature Reviews

Generally, research in heterogeneous catalysts is focused on the adsorption- and selective hydrogenation of α,β-unsaturated carbonyl compounds to produce various chemicals [21]. The selective C=O hydrogenation of α,β-unsaturated aldehydes toward unsaturated alcohol is importantly in the manufacture of pharmaceuticals, flavors and fragrances [1]. However, the C=C bond hydrogenation of α,β-unsaturated aldehydes toward saturated aldehydes is more favorable and can be achieved with high selectivity [2], while, hydrogenation of α,β-unsaturated aldehydes at C=O bond towards unsaturated alcohols is more difficult to achieve.

There are several researches that attempt to develop a suitable catalytic system for the selective hydrogenation of α,β-unsaturated aldehyde to unsaturated alcohol [21] because unsaturated alcohols is important in economic industrial system. Thus, study in preparation of new catalysts is essential for the preparation of unsaturated alcohols. A few articles in the literature show the use of noble metals deposited over supports for selective hydrogenation of α,β-unsaturated aldehydes and ester [24-25]. Conventional catalysts based on metals such as Ni, Pd or Rh are almost unselective towards unsaturated alcohols [21]. Although, Ru is moderately selective, and similar or better selectivities can be achieved with Os, Ir and Pt catalysts [26].

The selective hydrogenation of the C=O group of α,β-unsaturated aldehydes on the noble metals such as Pt is very difficult to achieve because the hydrogenation at C=C group is thermodynamically and kinetically favored, with the reason of strong hydrogenation activity of Pt [27].

As a catalyst with moderate hydrogenates activity, Cu has been used for the selective hydrogenation. Some researchers have reported the uses of oxide supports covered with a transition metal as catalysts for example Cu/MgO, Cu/C, Raney Ni, amorphous Ni alloys, Cu–Zn mixed oxides doped with Al, Mn, Fe, Rh, Ru, and Pt noble metals [28].

However, selective reactions are quite a problem when the C=C bond hydrogenation of α,β-unsaturated aldehyde is more favorable than C=O group. Since high costs of precious metals, their limited availability, and the decrease in selectivity at high temperatures [21] additionally, it was found that the deactivation rate in precious metal catalysts is high so they show low stability. Therefore, in order to improve the hydrogenation selectivity and stability of the catalyst, the carbonyl group C=O should be α,β-unsaturated aldehyde strongly adsorbed on the catalyst surface, and decreasing hydrogenation activity of C=C bond [21,28]. Among transition metal, Co

shows higher hydrogenation selectivity towards α,β-unsaturated alcohol than the noble metals such as Pt, Rh and Ru. In addition, several attempts have been made to improve the selectivity of the metal catalyst for the C=O bond hydrogenation by adding second elements: Sn, Mn and Fe, which have strong affinity for the C=O group [3]. Moreover, it was noticed that the yield in unsaturated alcohol is not only a specificity of the catalyst alone but also depends on the support.

In general, supported catalysts are very interesting materials because one metal can tune and/or modify the catalytic properties with the other transition metals [21]. Metallic catalysts are usually supported on high surface area carriers, such as: silica and alumina. Additionally, the preparation of supported metallic catalysts leads to the catalysts with new characteristics, where a specific interaction between the two metals leading to high selectivity towards unsaturated alcohols [5]. Several literatures reported that both vapor and liquid phase hydrogenation have been performed during the hydrogenation but the vapor phase hydrogenation is usually preferred because it can be carried out at normal atmospheric pressure and well-defined metal on surfaces [21].

C. Ando, et al. [3], studied the hydrogenation of (E)-2-hexenal with ethanol as a solvent over 40 wt.% Co/Al_2O_3 catalyst and bimetallic catalysts (Co-M, M= Pt, Pd, Ru, Rh, Cu, Fe, and Sn/Al_2O_3). Among the used metals, the activity and selectivity of unsaturated alcohol were improve by adding 0.1 wt.% Pt to Co/Al_2O_3. The addition of 0.1 wt.% Pt does not change the value of $Y_{C=C}$ appreciably and increased the value of $Y_{C=O}$ form 54.4% to 85.5%. However, when the Pt loading was raised to 1.0 wt.%, the selectivity to unsaturated alcohol is decreased with an increase of saturated alcohol and value of $Y_{C=C.}$ This suggest that Pt metal particles are formed at the higher metal loading and catalyzed the C=C bond hydrogenation.

S. Nishiyama, et al. [25], studied the selective hydrogenation of crotonaldehyde over SiO_2-supported monometallic Sn and bimetallic Rh-Sn catalysts in the liquid phase. Over a silica-supported monometallic Sn catalyst, no unsaturated alcohol was formed, whereas considerable amounts of the corresponding saturated aldehyde and saturated alcohol were obtained. The selectivity to the unsaturated alcohol was improved over the Rh-Sn bimetallic catalyst. The selectivity to the corresponding unsaturated alcohol is 65% over the Rh-Sn bimetallic catalysts.

A. Vicentea, et al. [41] investigate citral hydrogenation using Pd–Sn bimetallic catalysts at 130°C under 7 MPa and elucidating the structure–property relationships in this system. The modification of Pd monometallic catalysts by Sn favoured the selective hydrogenation of conjugated C=O bond, leading to the formation of nerol and geraniol (UA).

W. Yu, et al. [30], Amornpattana and Winterbottom [31] found that the activity and selectivity to unsaturated alcohol were improved considerable by adding Pt to Co/Al_2O_3. The addition of Pt does not change the value of $Y_{C=C}$, indicating that Pt in Co/Al_2O_3 enhance the activity for the C=O hydrogenation exclusively. The improvement of selectivity to unsaturated alcohol in the hydrogenation of unsaturated aldehyde was achieved by alloying Pt and Co [28]. In recently, improvement in activity and selectivity towards the unsaturated alcohol can be improved with the use of Pt-Sn catalysts. The promoter effect of Sn is attributed to ioniced Sn species which, acting as a Lewis acid, interacts with the oxygen atom of the carbonyl bond (basic group), thus weakening the C=O bond and favouring its hydrogenation [32].

G. K. Reddy, et al. [28] studied the activity of silica supported transition metal-based bimetallic catalysts ($M\text{-}M^1/SiO_2$ (M = Co, Ni, and Cu; M^1 = Ni, Cu, and Co)) for the vapour phase hydrogenation of furfuraldehyde. The $Cu–Co/SiO_2$ and $Ni–Cu/SiO_2$ combination catalysts exhibited a high selectivity towards the formation of furfuryl alcohol. Incorporation of silica support in the colloidal form during the deposition precipitation of bimetallics resulted in the stable and well-formed catalysts with high specific surface areas.

M. D. Porosoffb, et al. [2], studied controlling hydrogenation of C=O and C=C bonds in cinnamaldehyde using silica supported Co-Pt and Cu-Pt bimetallic catalysts. The reactor evaluation results show that Co-Pt and Cu-Pt bimetallic catalysts exhibit much higher hydrogenation activity than the corresponding monometallic catalysts, and Co-Pt shows much higher selectivity towards C=O bond hydrogenation than Cu-Pt. The trend of hydrogenation activity and selectivity is consistent with previous studies of the hydrogenation of unsaturated aldehydes on model bimetallic surfaces.

B. M. Re[illegible]ya [21], studied hydrogenation of cinnamaldehyde in the vapour phase at normal atmospheric pressure over silica supported transition metal-based bimetallic catalysts ($M–M1/SiO_2$ (M = Co, Ni, and Cu; M1 = Ni, Cu, and Co)). Among the various catalysts investigated, the $Cu–Co/SiO_2$ combination catalyst exhibited very promising results for the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol, whereas $Co–Ni/SiO_2$ and $Ni–Cu/SiO_2$ bimetallic catalysts provided good yields of hydrocinnamaldehyde.

F. Djerbouaa, et al. [5], suggested that the highest selectivity to crotyl alcohol (~90%) was obtained in hydrogenation of crotonaldehyde using 40 wt.% Co/SiO_2 catalyst calcined at 400°C and reduced at 350°C even at conversions as high as 60%. Higher temperature of calcination was found to lower the crotyl alcohol selectivity.

In this study, a series of transition metal cobalt-based silica catalyst (M–Co/SiO_2, M = Pt, Fe, and Cu) was prepared by wetness impregnation method and investigated for hydrogenation of 2-hexenal to 2-hexenol in the vapor phase at normal atmospheric pressure. In addition, these catalysts were characterized by BET, XRD, CO_2-TPD and TPR techniques. The effect of reaction conditions in fixed-bed reactor: type of solvent, contact time, and reaction temperature were also studied in order to obtain the appropriate catalyst and reaction conditions for the selective hydrogenation of 2-hexenal.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Gases and Chemicals

1. Air zero gas, high purity (99.99%), PRAXAIR
2. Hydrogen gas, high purity (99.99%), PRAXAIR
3. Nitrogen gas, high purity (99.99%), PRAXAIR
4. Deionized water
5. Precipitated silica (SiO_2), 99.0%, CARLO ERBA
6. Cyclohexane, ACS for analysis, CARLO ERBA
7. 2-hexenal ($C_6H_{10}O$), 98%, ALDRICH
8. Copper(II)acetate monohydrate($Cu(CH_3COO)_2H_2O$), AR Grade, QRec
9. Iron(III)nitrate nanohydrate ($Fe(NO_3)_39H_2O$), AR Grade, QRec
10. Chloroplatinic acid hexahydrate ($H_2PtCl_6(H_2O)_6$), Sigma-ALDRICH
11. Cobalt nitrate hexahydrate ($Co(NO_3)_26H_2O$), 99.0%, CARLO ERBA

3.2 Apparatus and instruments

1. Catalytic testing rig
2. Mass flow controller (GFC 17, Aalborg)
3. Oven
4. Tube furnace with a programmed temperature controller (MTF 12/25/250, Carbolite)
5. Heating tape with a programmed temperature controller
6. Clamp
7. Gas chromatograph (Model 910, Buck scientific)
8. Laboratory glassware
9. Laboratory plasticware
10. Trap condenser
11. Vial
12. Sieve (U.S.A standard sieve, AASHO N-92)
13. X-ray Powder Diffractometer (D8 advance, Bruker AG)
14. Gas adsorption analysis (Autosorb-1C, Quantachrome)

15. Temperature programmed reduction (TPR, Model TCD2-NIFED)

3.3 Experimental

3.3.1 Preparation of Metal-Cobalt Based Supported Silica Catalysts (M-Co/SiO_2)

The metal-cobalt based supported silica (SiO_2) catalysts with different type of loaded metals (Fe, Pt, and Cu) were prepared by wet impregnation method.

In the first step, 20 wt.% Co supported on SiO_2 (Co/SiO_2) was prepared by wet impregnation method using cobalt nitrate hexahydrate ($Co(NO_3)_26H_2O$) precursor. In this step, the wetted SiO_2 support after addition of few deionized water, was impregnated with a solution of Co precursor. After that, it was dried in oven at 60°C for 24 hours. Then, the dried catalyst was grinded into fine powders and was calcined in a horizontal tube furnace under a flow of air zero (60 ml/min) at 400°C for 5 hours with heating rate at 2°C /min.

In the second step, a series of metal-cobalt/SiO_2 catalysts with different metal loaded: Fe, Cu, and Pt was subsequently prepared by wet impregnation with 10 wt.% Fe, 10 wt.% Cu, and 0.1wt.% Pt using $Fe(NO_3)_39H_2O$, $Cu(CH_3COO)_2H_2O$, and $H_2PtCl_6(H_2O)_6$, respectively. In a typical procedure, those metal-Co/SiO_2 catalysts were prepared by slowly drop metal solution into Co/SiO_2, which was prepared from the first step, until it seem wet, and dried in an oven at 60°C for 5 hours. The process was repeated until all metal precursor solution is consumed. The prepared catalyst was calcined in a horizontal tube furnace under a flow of air zero (60 ml/min) at 400°C with a heating rate of 2°C/min and hold at that temperature for 5 hours. Finally, the catalyst was pressed, crushed, and sieved into 600-850 μm.

3.3.2 Characterization of catalysts

3.3.2.1 X-Ray powder diffraction

The structure of catalyst was determined by X-ray diffractometer (XRD) (D8 Advance, Bruker, Scienctific Instrument Service Centre, KMITL). The sample was prepared by packing the catalyst into the sample holder. CuK_α X-ray beam was used for analysis at 30 kv and 30 mA. The sample was scanned over the angle ranged from 2θ: 5° to 80° with 1 second/step time and 0.04 2θ/step increments. X-ray diffraction pattern of the sample was compared with the X-ray diffraction pattern of standard catalyst for structure determination.

3.3.2.2 Surface area analysis

Surface area of the catalyst was determined by surface area analyzer (Autosorb-1C, Quantachrome). The sample was prepared by weighing approximately 40-50 mg of sample and loaded into a cleaned and dried sample cell. After that, the sample was degassed at out-gas station at 350°C for 24 hours. The sample cell was then removed from the out-gassing station after nitrogen was filled and was attached to the analysis station. The adsorption isotherm was measured in a pressure range of 0.05-0.30 P/P_0 at -196°C.

3.3.2.3 Temperature programmed reduction

Temperature-programmed reduction (TPR) provides information on the active site species of the catalysts by monitoring their reducibility. Temperature programmed reduction was measured using thermal conductivity detector (TCD). The sample weighed 50 mg was placed into a quartz tube reactor, which was located inside a temperature-regulated furnace. Prior to the H_2-TPR, each sample was heated to its calcinations temperature in air zero (30 ml/min) for 5 hours and was cooled down to 40°C. The heating rate of 5°C/min, 30 ml/min of 10% H_2 in Ar was applied for TPR analysis. Water production during the reduction process was removed in a U-shape glass trap at -77°C (vapor of liquid N_2) before entering the TCD.

3.3.2.4 Temperature programmed desorption

Basic sites of the catalysts were evaluated on the basis of temperature-programmed desorption of carbon dioxide (CO_2-TPD). Samples were pretreated by calcinations at 400°C under a flow of Air-Zero (30 ml/min) for 180 min and reduction at 400°C under a flow of H_2 (30 ml/min) for 120 min in order to reduce Co (II, III) to Co(0), then CO_2 was introduced at a flow rate of 40 ml/min at 30°C for 1 h. The physisorbed CO_2 was removed at 30°C by He for 1 h. After that, the CO_2-TPD profiles were obtained by heating sample at a rate of 10°C /min in a flow of He (30 ml/min).

3.3.3 Catalytic Testing

Gas phase catalytic conversion of 2-hexenal was investigated at atmospheric pressure in a continuous fixed-bed reactor made with glass tube (8.0 mm O.D.). Schemattic of the catalytic testing rig is shown in Figure 3.1. The catalyst bed was packed in the middle of the reactor and close with glass wool and glass beads. After that, the reactor was installed onto the catalytic test

rig, which was located inside a temperature-controlled electrical furnace. The gas flows were controlled by the mass flow controllers and checked by bubble flow meter. Before the testing, the catalyst was activated by heating at 5°C/min to its calcinations temperature at 400°C and was held at that temperature for 3 hours under the stream of air zero (30 ml/min), then N_2 was flowed to eliminate remaining air zero in line. Finally, it was switched to a flow of H_2 gas for reduction with a heating of 5°C/min to 400°C and hold for 2 hours. The reactor was cooled down to the reaction temperature at 80°C.

In each run, 2-hexenal was passed through the catalyst bed by a 30 ml/min flow of H_2. The catalytic testing was continued for at least 6 hours on stream. The reacted gaseous mixture was flowed out of the reactor and passed through a gas sampling loop. In order to prevent condensation of products, the line after reactor was heated by heating tape. Description of the reactor set up and the reaction conditions are summarized in Table 3.1.

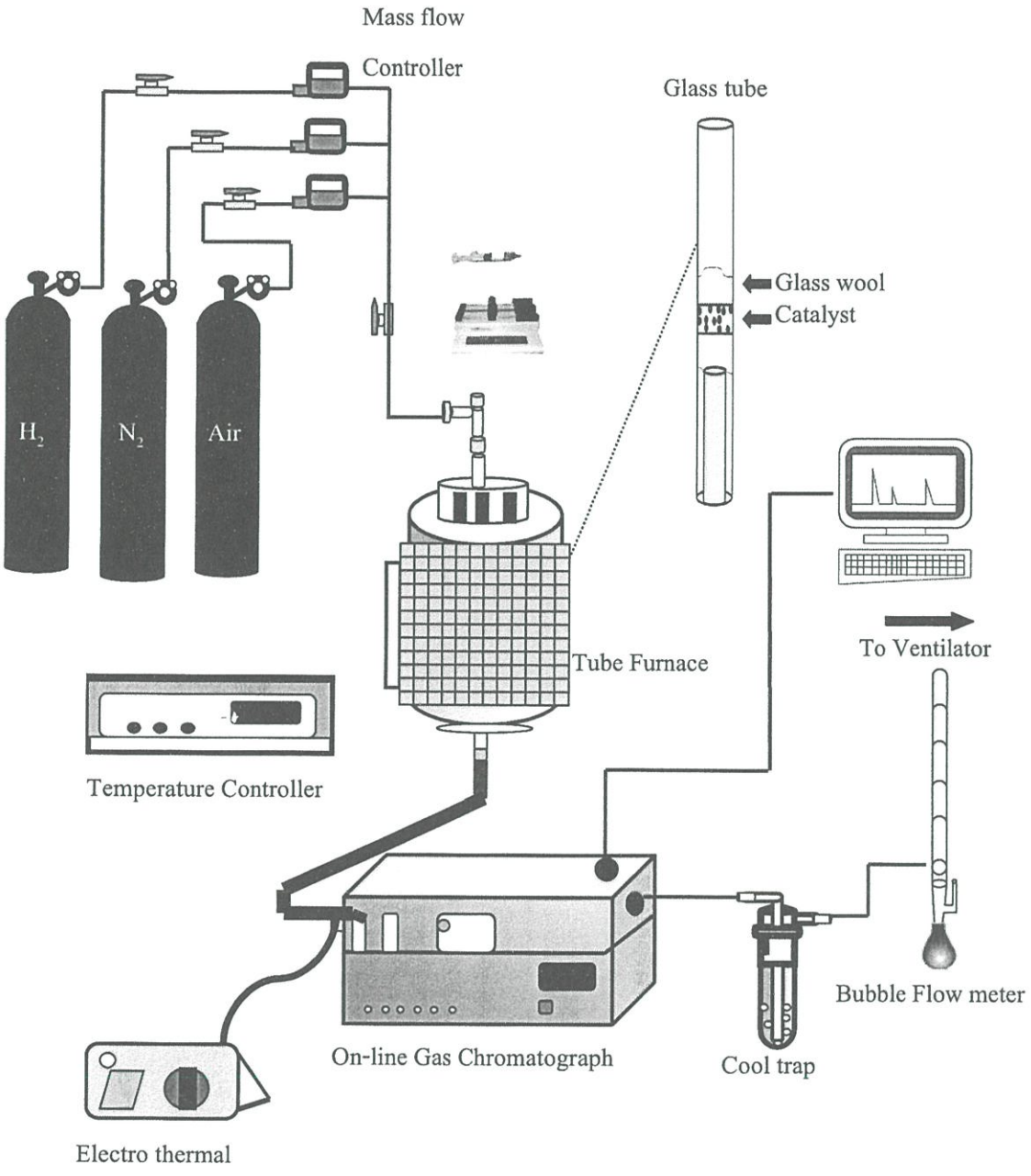


Figure 3.1 Schematic of the catalytic testing rig for selective hydrogenation of 2-hexenal

Table 3.1 Description of the reactor set up and the reaction condition

Parameters	Value
Reactor outside diameter (mm)	8
Bed length (mm)	10
Total flow (ml/min)	30
Catalyst weight (g)	0.15
Contact time: W/F (g.h/mol)	30-500
Catalytic size (μm)	600-850
Catalyst activation (before reaction)	Heating rate: 5°C/min Calcination temperature: 400°C Gas: air zero (30 ml/min)
Catalyst reduction (before reaction)	Heating rate: 5°C/min Reduction temperature: 400°C Gas: Hydrogen (30 ml/min)
Reaction temperature	80°C
Reaction total pressure	Atmospheric pressure (1 atm)

3.3.4 Products analysis

The product analysis was generally performed using an online gas chromatograph. The gas sample was collected in gas sampling loop, then periodically injected into GC column (Carbowax, 30 m length, 0.32 mm internal diameter, 0.25μm film thickness) connected to flame ionized detectors (FID). Each components were separated as they pass though the column with an inert carrier N_2 gas and their presence in the effluent were recorded as a chromatogram. Each peak areas from the chromatogram was measured and calculated. Then each peak was identified

by comparing with standard and the composition of each products were determined by calibration of standard.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Characterization of Co/SiO_2, $CoPt/SiO_2$, $CoCu/SiO_2$, and $CoFe/SiO_2$

4.1.1 Gas Adsorption Characteristics

The specific surface area, pore volume, and pore size diameter of the catalysts were determined by BET measurements using N_2 gas adsorption analyzer. The result is shown in **Table 4.1**

Table 4.1 Textural properties of the SiO_2, Co/SiO_2, and $Co\text{-}M/SiO_2$ catalysts

Sample	S_{BET} [a] (m^2/g)	[b]Pore volume (ml/g)	[c]Average pore diameter (nm)
SiO_2	242	0.80	10
Co/SiO_2	201	0.98	16
$CoPt/SiO_2$	207	1.09	17
$CoCu/SiO_2$	184	0.90	16
$CoFe/SiO_2$	187	0.76	14

[a]S_{BET} : specific surface area determined by BET method

[b]Cumulative desorption pore volume by BJH method

[C]Desorption pore diameter by BJH method

As expected, a prompt decreased in surface area can be observed after the addition of 10 wt.% Fe or Cu into monometallic Co/SiO_2 catalyst. It can be suggested that the incorporated metals has low surface area. No significant change in the surface area can be observed when the monometallic Co/SiO_2 catalyst was added with 0.1 wt.% Pt. In addition, the pore volumes and average pore diameters of all catalysts remain the same after the addition of Pt, Cu, and Fe.

4.1.2 X-Ray Powder Diffraction (XRD)

The catalysts prepared by impregnation method after calcined at 400°C were determined by X-ray powder diffraction technique (XRD), using CuK_α as radiation source at 30 kv,30 mA. In order to identify the crystal structure, 2θ angles in XRD diffraction pattern of each catalysts were compared with those of the reference diffraction pattern. The catalysts were scanned over the angle range (2θ) from 5° to 80° as shown in **Figure 4.1**.

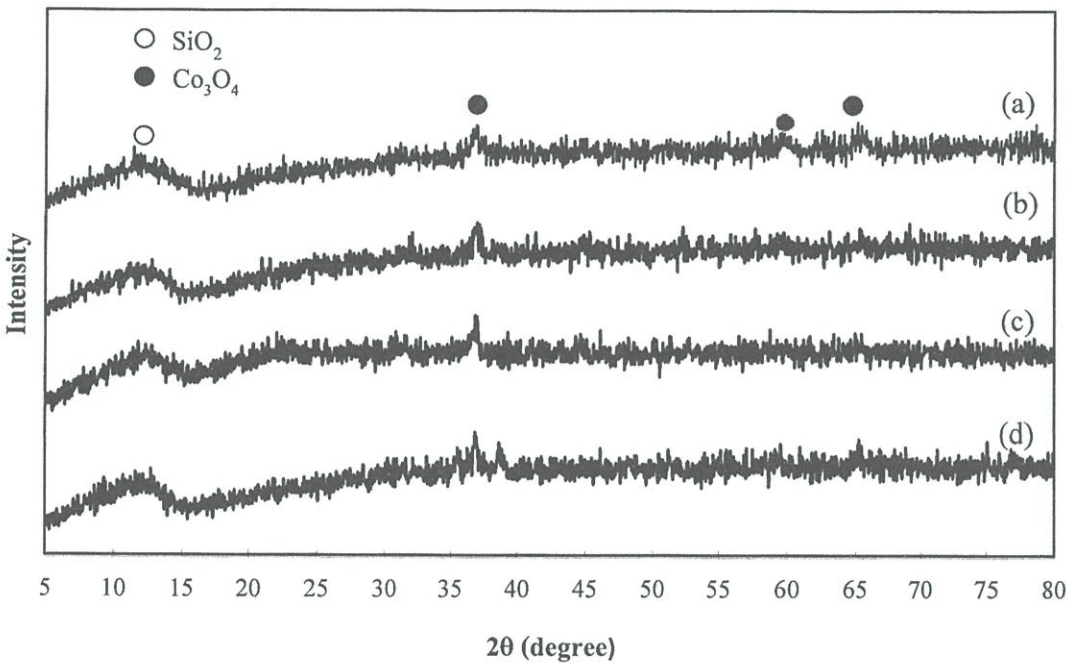


Figure4.1 XRD patterns of Co/SiO_2 (a), $CoPt/SiO_2$(b), $CoCu/SiO_2$(c), and $CoFe/SiO_2$(d) catalysts.

As seen from Figure 4.1, all catalysts show a broad peak at 2θ around 13.4°, which can be attributed to an amorphous SiO_2 [33]. Moreover, the catalysts also showed the diffraction peak at 37.8°, 59.3°, and 65.2°, which indicates the presence of cobalt in the form of crystalline Co_3O_4 phase after calcination at 400°C [33]. However, a decrease in the intensity and broadening of these diffraction peaks can be observed upon the incorporation of the other metals. Interestingly, no diffraction lines corresponding to the oxides of Pt, Cu, or Fe can be observed. This is probably due to their small particle sizes and high dispersion of the incorporated metal oxide phase, which was obscured by the diffraction peak of amorphous SiO_2 or below the detection limit of XRD [33].

4.1.3 Temperature program reduction (TPR)

The H_2-TPR profile of catalysts prepared by impregnation method with different metal loaded are compared as shown in **Figure 4.2**.

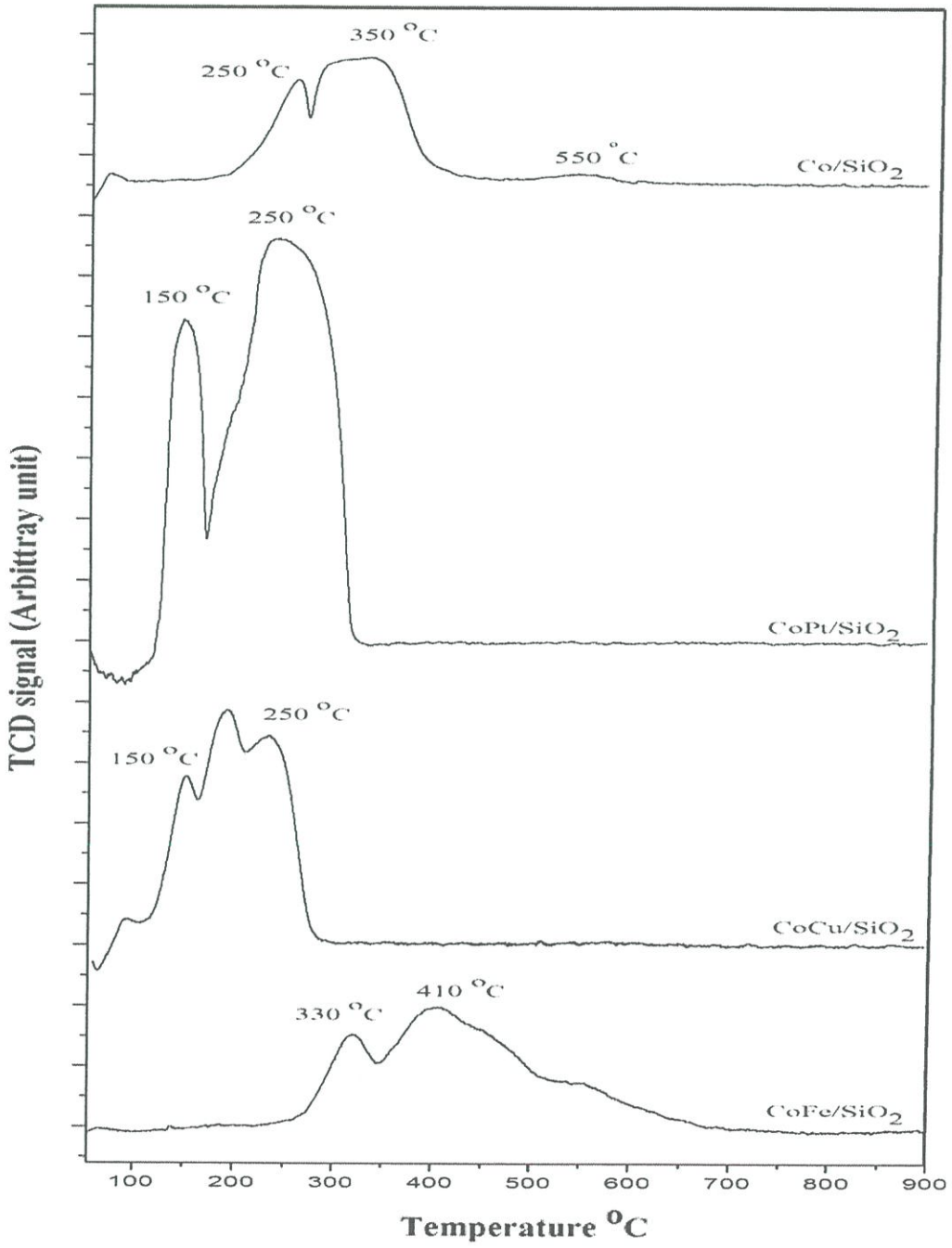


Figure 4.2 TPR profiles of Co/SiO_2 and $M\text{-}Co/SiO_2$ catalysts (10 % H_2/Ar, ramping at 5°C/min).

As seen from Figure 4.2, Co/SiO_2 shows two main reduction peaks at the temperature of 250°C and 350 °C. The first peak is assigned to the reduction of Co_3O_4 to CoO, and the second one is the subsequent reduction of CoO to metallic Co, respectively [34]. In addition, shoulder reduction peak around 550-600°C is observed, which suggests the reduction of cobalt silicate species that requires high reduction temperature. When copper was added into Co/SiO_2 catalyst, it is found that the reduction temperature of cobalt shift to lower temperature (120-280°C), indicating the partial formation of cobalt-copper alloy phase on the SiO_2 support [34]. In addition, the formation of cobalt-platinum alloy phase on SiO_2 support (250°C), is also observed after incorporation of platinum to Co/SiO_2 [35]. Therefore, incorporation of platinum and copper to Co/SiO_2 facilitate reduction of cobalt. On the other hand, in the case of $CoFe/SiO_2$ catalyst, it exhibited a broad peak located between the TPR peaks of Co/SiO_2 and Fe/SiO_2 (around 280-650°C) [34, 36], indicating the formation of cobalt-iron alloy on SiO_2 support. It is note that less H_2 consumption is obtained for $CoFe/SiO_2$ catalyst. This indicates that iron oxide cannot be completely reduced.

4.1.4 Temperature Programmed Desorption (TPD)

The desorbed CO_2 was detected by TCD. The CO_2-TPD profiles of Co/SiO_2 and $CoCu/SiO_2$ catalysts are shown in **Figure 4.3**

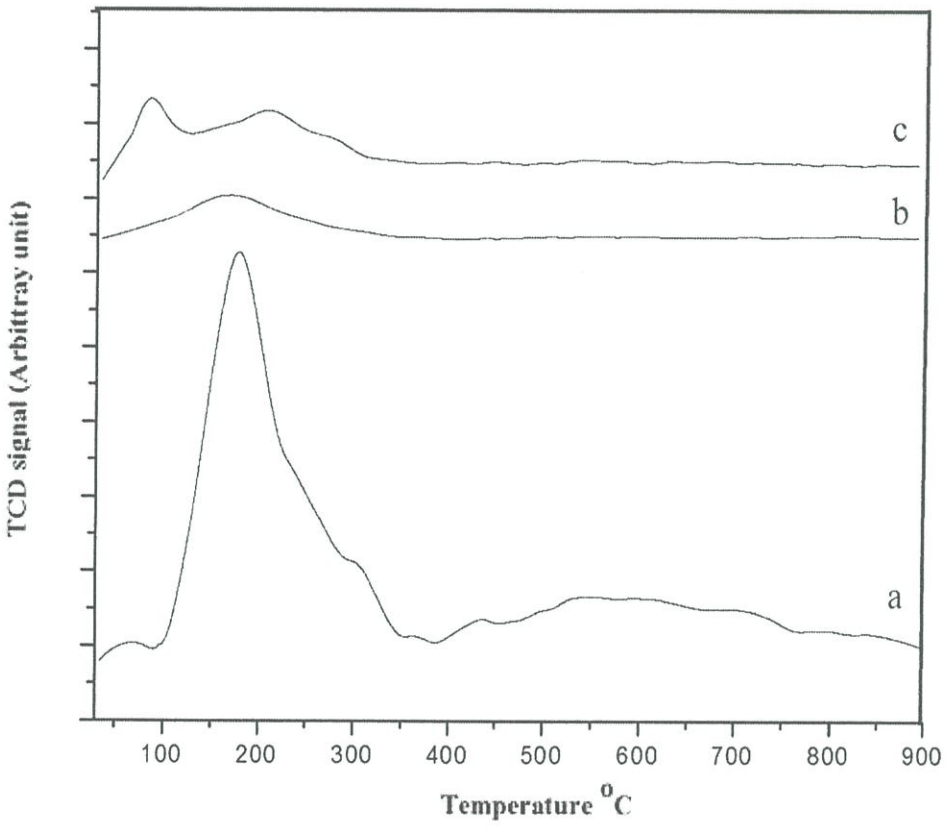


Figure 4.3 TPD profiles of Co/SiO_2 reduced at 400°C (a), 700°C (b), and $CoCu/SiO_2$ catalyst (c).

The Co/SiO_2 reduced at 400°C (Figure 4.3(a)) shows the CO_2 desorption peak at temperature range of 100°C to 250°C, which is attributed to the adsorption of CO_2 on the cobalt silicate [37]. In addition, high temperature desorption peak (400°C–900°C) is attributed to cobalt carbonate formed by strong interaction between cobalt silicate and CO_2. As the cobalt silicate is reduced at 700°C, significant reduction in CO_2 adsorption can be observed for Co/SiO_2 (Figure 4.3(b)). However, $CoCu/SiO_2$ catalyst does not show significant basicity. This is because, most of the cobalt becomes CoCu alloy as seen by TPR, and no cobalt silicate was formed. Moreover, incorporation of copper can also increase the acidity (Figure 4.3(c)) [38-39].

4.2 Study of 2-hexenal conversion

Products distribution of 2-hexenal conversion over $CoPt/SiO_2$ catalyst

The conversion of 2-hexenal over $CoPt/SiO_2$ catalyst and yield of products at various contact time are shown in **Figure 4.4.**

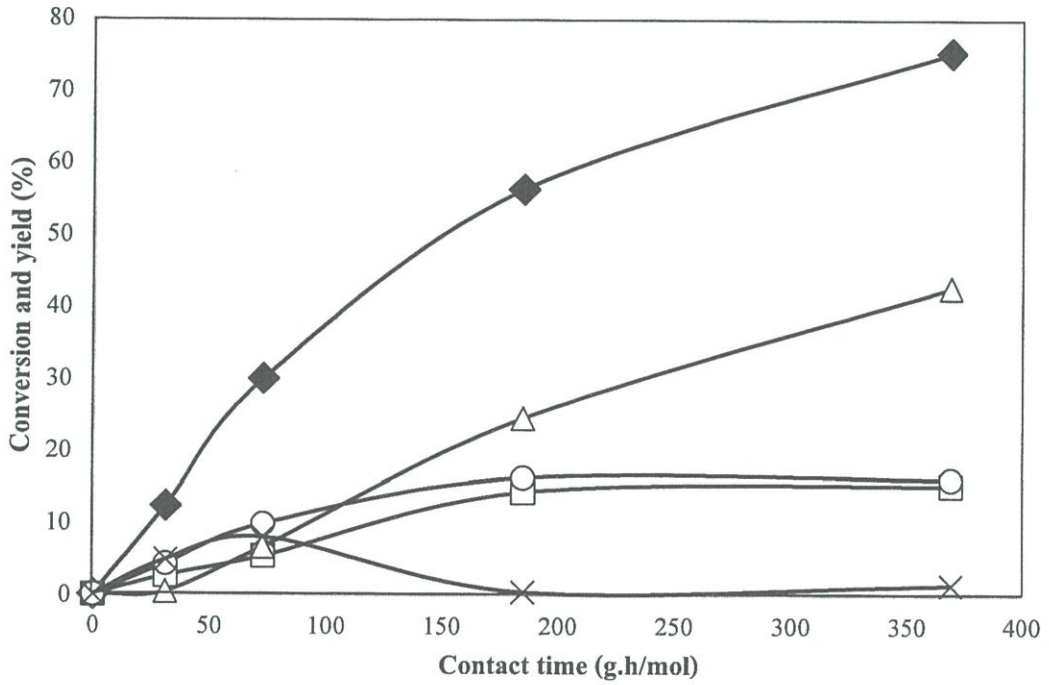


Figure 4.4 Conversion of 2-hexenal (◆) and yields of product (hexanal (□), hexanol (△), 2-hexenol (○) and aldol (X))

**Reaction condition; Catalyst: $CoPt/SiO_2$, Solvent: cyclohexane, Temperature: 80 °C, Flow rate of feed plus carrier gas: 30 ml/min, Pressure: 1 atm, Contact time: 31-369 g.h/mol. The results were an average of the fourth and the fifth hours of time on stream (steady state).*

It can be seen that the conversion of 2-hexenal is increased with contact time. The result is generally expected since increasing contact time allows a better chance for the reactant to interact with the catalyst active sites. Considering the products yield, it is observed that at very low contact time, the 2-hexenal can be converted to 2-hexenol and hexanal via hydrogenation of

C=O and C=C bond, respectively. This indicates that 2-hexenol and hexanal are generated in parallel. At the same time, hexanal may undergo aldol-condensation to high molecular weight compounds over basic sites (as evidenced by TPD-CO_2) of the cobalt-based catalysts. As the contact time is increased, the hexanol yield is noticeably increased while yield of hexanal and 2-hexenol appear to be unchanged. This suggests that the both 2-hexenol and hexanal may be hydrogenated to hexanol. The overall reaction pathway can be proposed in **Figure 4.5**.

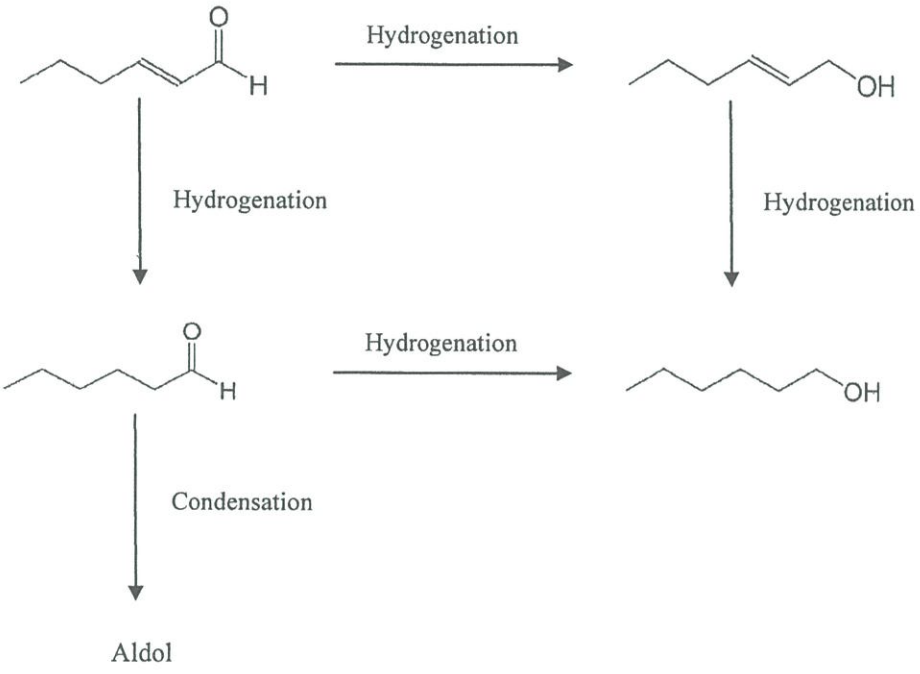


Figure 4.5 The proposed reaction scheme for 2-hexenal conversion over CoPt/SiO_2 catalyst

It is noteworthy that at high contact time, the aldol product was not found because hexanal was mostly converted to hexanol. Hence, the aldol-condensation of hexanal was limited. However, the initial decline of the hydrogenation activity is observed, particularly in the reaction at high contact time as shown in **Figure 4.6.**

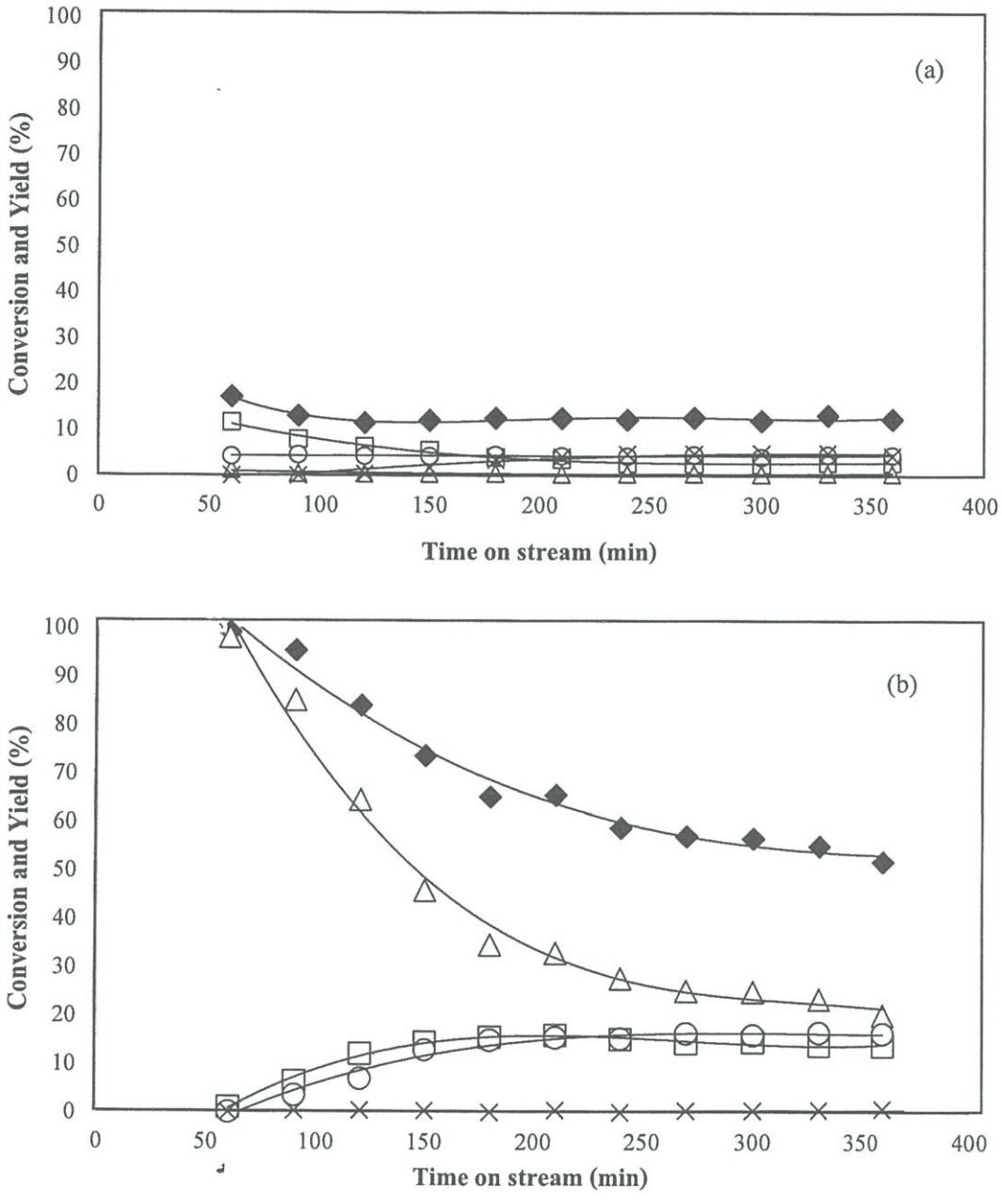


Figure 4.6 Conversion of 2-hexenal (◆) and yields of product (hexanal (□), hexanol (△), 2-hexenol (○) and aldol (X)) at contact time of 31 g.h/mol (a) and 185 g.h/mol (b).

**Reaction condition; Catalyst: $CoPt/SiO_2$, Solvent: cyclohexane, Temperature: 80°C, Flow rate of feed plus carrier gas: 30 ml/min, Pressure: 1 atm, Contact time: 31g.h/mol and 185 g.h/mol*

At high contact time (Figure 4.6 (b)), hexanol was mostly found at the initial state due to the saturation of hydrogen on the metal surface. However, the hexanol is slowly decreased, suggesting the competitive adsorption between the reactant and hydrogen on the catalyst surface before reaching a steady state. In turn, a steady state can be rapidly reached for the reaction with lower contact time (Figure 4.6 (a)) as there is higher concentration of the reactant, as compared with the available active sites.

A non-steady state of the reaction can be verified by an experiment that the feed is withdrawn and re-injected as shown in **Figure 4.7**

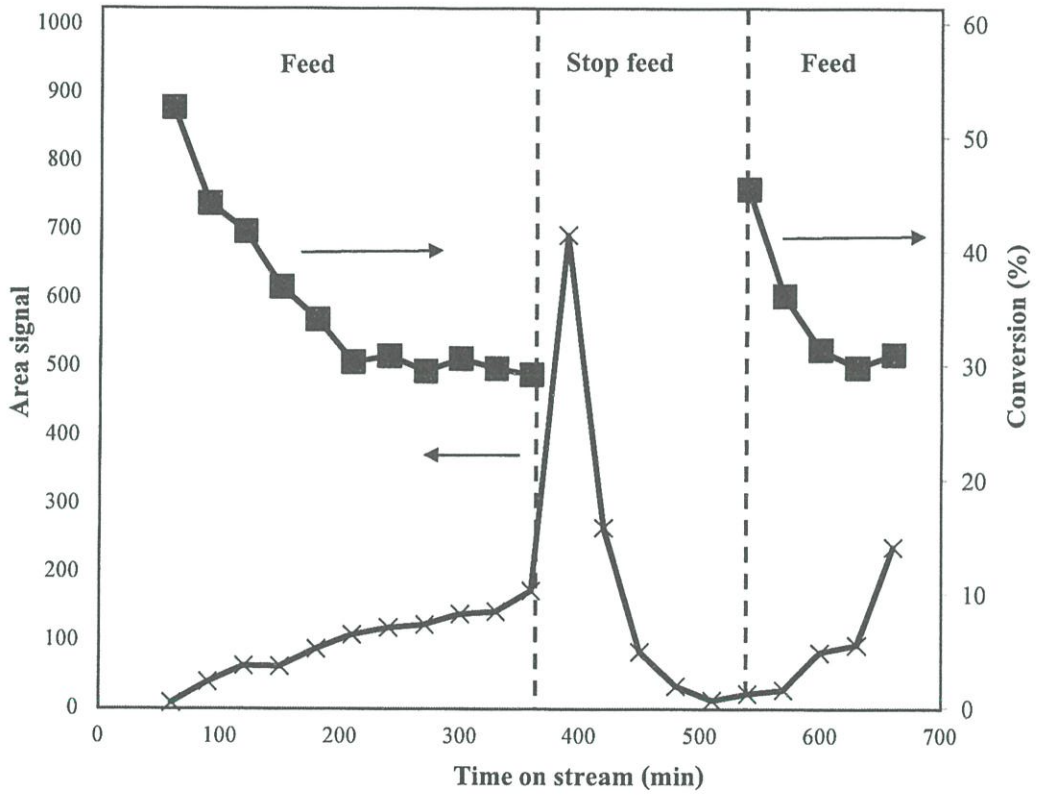


Figure 4.7 Conversion (■) and area signal of high molecular weight compound (X)

**Reaction condition; Catalyst: $CoPt/SiO_2$, Solvent: cyclohexane, Temperature: 80°C, Flow rate of feed plus carrier gas: 30 ml/min, Pressure: 1 atm, Contact time: 73 g.h/mol.*

It can be seen that high molecular weight compounds were desorbed when the feed is removed (during 360-540 minutes on stream). It is suggested that there are high molecular weight products forming on surface of the catalyst during the reaction. After the surface is cleaned and saturated with hydrogen, an enhance activity is recovered when the feed is re-injected. The

activity then declined in a manner similar to that at the initial test and retained at the same level of conversion. Accordingly, no permanent deactivation takes place on the catalyst under the reaction condition investigated.

Influence of metal loaded over Co/SiO_2 catalyst

The effect of metal incorporated in Co/SiO_2 catalyst ($CoPt/SiO_2$, $CoCu/SiO_2$, and $CoFe/SiO_2$) on 2-hexenal conversion was investigated as shown in **Table 4.2.**

Table 4.2 Conversion of 2-hexenal over Co/SiO_2, $CoPt/SiO_2$, $CoCu/SiO_2$, and $CoFe/SiO_2$ catalysts.

Catalyst	Conversion	Selectivity (%)			
	(%)	hexanal	hexanol	2-hexenol	aldol
Co/SiO_2	26.3	29.3	29.4	31.3	10.0
$CoPt/SiO_2$	38.3	21.4	33.7	28.1	16.8
$CoCu/SiO_2$	13.6	40.2	5.2	12.1	42.5
$CoFe/SiO_2$	14.6	23.1	19.6	13.2	44.1

**Reaction condition; Contact time: 73 g.h/mol, Carrier gas : H_2, Temperature: 80°C, Flow rate of feed plus carrier gas: 30 ml/min, Pressure: 1 atm. The result were an average.*

It was observed that $CoCu/SiO_2$ and $CoFe/SiO_2$ catalysts give low conversion to the hydrogenated products, (hexanal, hexanol, and 2-hexenol). However, aldol-condensation to higher molecular weight compound is promoted over these catalysts, as shown by the yield of aldol product in **Figure 4.8**.

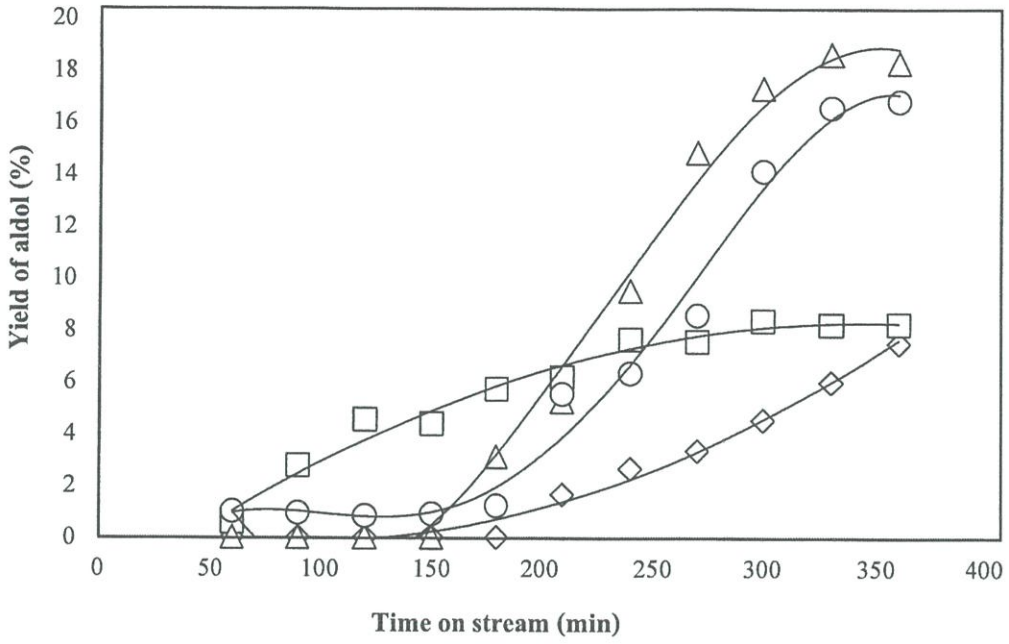


Figure 4.8 Yield of aldol over Co/SiO_2 (◇), $CoPt/SiO_2$ (□), $CoCu/SiO_2$ (○) and $CoFe/SiO_2$ (△).

**Reaction condition; Contact time: 73 g.h/mol, Carrier gas:H_2, Temperature: 80°C, Flow rate of feed plus carrier gas: 30 ml/min, Pressure: 1 atm.*

It is well known that the activity of a hydrogenation catalyst is related to the reducibility of the metal [40]. As iron is not completely reduced to Fe^0 at 400°C and CoFe alloy was partially formed as shown in TPR result (Figure 4.2), irreducible CoFe mixed oxide and iron oxide species shall remain on the catalyst surface. These species are oxophilic and inactive for hydrogenation [9]. However, they can promote a strong interaction between the catalyst and hexanal leading to aldol condensation of the hexanal. In the case of $CoCu/SiO_2$, TPR result indicated that at 400°C, the catalyst was completely reduced and CoCu alloy was formed. However, dissociation of hydrogen on the CoCu alloy is less effective, as compared to the metallic cobalt alone. Hence, the hydrogenation activity is reduced. In addition, the alloy CoCu on silica enhances surface acidity of the catalyst [38, 39]. This can be seen by low CO_2 adsorption experiment (CO_2-TPD, Figure 4.3). Such the surface acidity can promote higher yield of aldol product as observed [37].

When platinum is incorporated in the Co/SiO_2, the higher activity is obtained as compared to the parent and other metal loaded catalysts. This is due to the presence of active of platinum metal even only 0.1 wt.%. However, the selectivity of 2-hexenol, a desired product, was

similar in both $CoPt/SiO_2$ and Co/SiO_2 catalysts. In order to verify the selectivity of these catalysts, a similar level of conversion is compared as presented in **Table 4.3.**

Table 4.3 Comparison of 2-hexenol selectivity at similar level of conversion over Co/SiO_2 and $CoPt/SiO_2$

Catalyst	Conversion (%)	Selectivity (%)
Co/SiO_2	20.8	34.2
$CoPt/SiO_2$	18.9	37.6

**Reaction condition; Carrier gas:H_2, Temperature: 80 ^{o}C, Flow rate of feed plus carrier gas: 30 ml/min, Pressure: 1 atm. The result at 210 minutes on stream. Contact time: 73 g.h/mol.*

It can be seen that $CoPt/SiO_2$ catalyst exhibits slightly higher selectivity towards 2-hexenol. This selective hydrogenation of C=O bond of the $CoPt/SiO_2$ can be explained by the electron deficiency of the cobalt. As seen by TPR, CoPt alloy is formed and electron transfer is expected from cobalt to platinum [9, 40] (TPR result, Figure 4.2). This electron deficiency results in strong adsorption of lone pair electron of the carbonyl group [40]. Accordingly, higher selectivity for hydrogenation at the carbonyl group is promoted over CoPt alloy catalyst.

Influence of solvent on hydrogenation of 2-hexenal over $CoPt/SiO_2$

The effect of solvent on the conversion of 2-hexenal and products yield was investigated over $CoPt/SiO_2$ as shown in **Figure 4.9.**

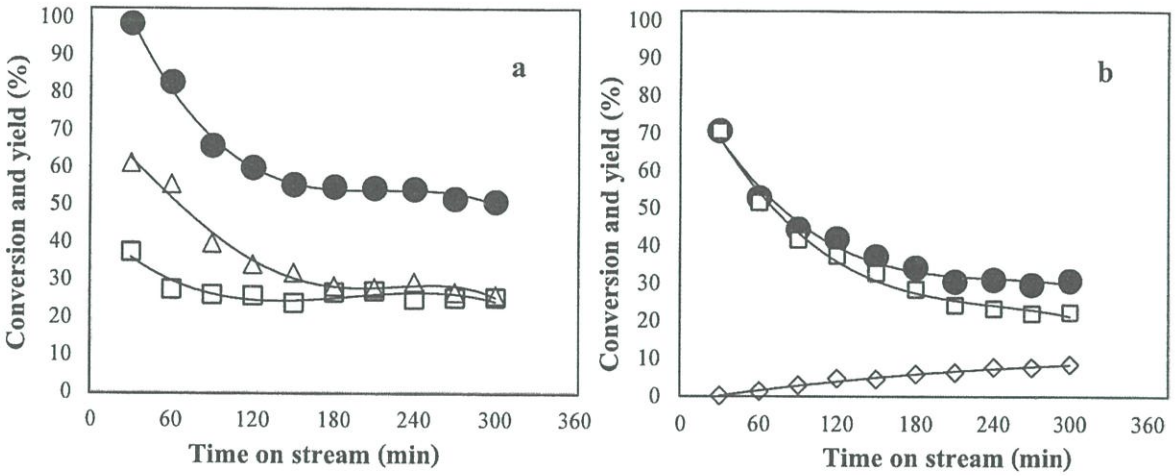


Figure 4.9 Comparison of the conversion of 2-hexenal (●), yield of hydrogenation product (□), yield isomer of 2-hexenal (△), and yield of aldol product (◇) in methanol (**a**) and in cyclohexane solvent (**b**).

** Reaction condition ; CoPt/SiO2, solvent : methanol and cyclohexane, Temperature 80 °C Flow rate of feed plus carrier gas : 30 ml/min, Pressure: 1 atm, Contact time: 73 g.h/mol.*

As seen in **Figure 4.9**, the hydrogenation of 2-hexenal over $CoPt/SiO_2$ using methanol as a solvent, exhibits higher conversion, as compared with that using cyclohexane as solvent. However, less yield of hydrogenated product it observed, while an isomer of 2-hexenal were obtained as main product. In contrast, all conversion of the 2-hexenal using cyclohexane as a solvent give only hydrogenated products. It is suggested that methanol is a polar solvent that may remain as liquid films on catalyst surface and induce polarization of 2-hexenal. This facilitated isomerization of 2-hexenal leading to an observed high conversion. Possible isomers (from GC-MS) from isomerization product are proposed in **Figure 4.10**.

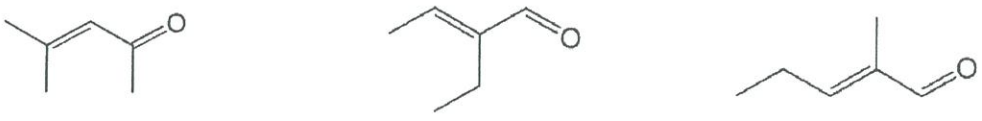


Figure 4.10 Proposed isomerization products of 2-hexenal

This solvation effect in methanol solvent can be reduced by an increase in reaction temperature as shown in **Figure 4.11**.

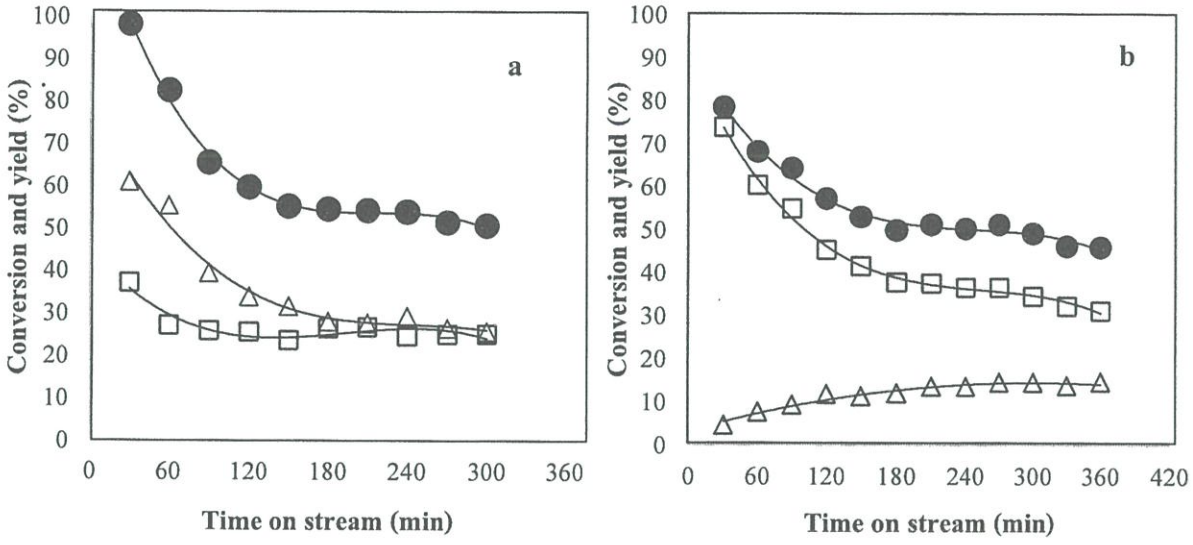


Figure 4.11 Comparison of the conversion of 2-hexenal (●), yield of hydrogenation product (□), and yield isomer of 2-hexenal (△) using methanol as a solvent at 80°C (**a**) and 120°C (**b**).

** Reaction condition ; $CoPt/SiO_2$, solvent : methanol , Temperature 80°C and 120 °C Flow rate of feed plus carrier gas : 30 ml/min, Pressure: 1 atm, Contact time: 73 g.h/mol*

It can be seen that isomer of 2-hexenal is reduced as reaction temperature is increased. This is because at 120°C polarization by gas phase methanol is somewhat reduced. Hence, isomerization was not induced. It is noteworthy that, using methanol as a solvent, no aldol product was obtained. This is due to the silanol group of silica supports that can interact methanol. Thus, this competitive adsorption of methanol against hexanal on the catalyst surface, hindering the conversion of hexanal to aldol products. In contrast, cyclohexane would not interacted with silanol group. This is because cyclohexane as non-polar solvent.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

The hydrogenation of 2-hexenal was investigated over Co/SiO_2 and metal loaded Co/SiO_2 catalysts (Pt, Fe, and Cu). The surface area of metal loaded catalysts particularly (Cu and Fe) was reduced, as compared to the Co/SiO_2 catalyst. The diffraction patterns of the catalysts show amorphous silica and cobalt oxide phase (Co_3O_4). No diffraction peaks of the Pt, Cu, or Fe oxides were observed, presumably due to the high dispersion of the incorporated metal oxide phase. Cobalt silicate formed in Co/SiO_2 exhibited basicity. Cobalt-metal alloy phase particularly CoCu and CoPt were formed after reduction at 400°C. On the other hand, CoFe alloy was partially formed on $CoFe/SiO_2$ catalyst and CoFe mixed oxide, iron oxide are remained on the surface of this catalyst.

It was found that over the $CoPt/SiO_2$, 2-hexenol and hexanal were obtained in parallel as primary products via hydrogenation of C=O and C=C bond, respectively. The catalyst show high selectivity to 2-hexenol, as compared to hexanal. Both 2-hexenol and hexanal can be further hydrogenated to hexanol. In addition, hexanal can be converted to high molecular weight products via aldol-condensation over the basic site of the catalyst. The CoPt alloy formed is more selective for hydrogenation at the carbonyl group. The CoFe alloy is inactive for hydrogenation and promotes undesirable aldol-condensation. This is due to strong interaction of the hexanal with the oxophilic surface of $CoFe/SiO_2$ catalyst. The CoCu alloy is relatively low in hydrogenation activity and promotes aldol-condensation presumably due to its acidity. Using methanol as a solvent induces polarization of the reactant, facilitating isomerization of the 2-hexenal. Solvation effect can be reduced by increasing reaction temperature. In addition, the competitive adsorption of methanol on the catalyst surface prevents the conversion of hexanal to aldol products.

5.2 Suggestions for future studies

1. It is interesting that increase H_2 partial pressure may well affect the H_2 dissociation over the catalyst. Effect of H_2 partial pressure should be studied.

2. Due to limit of reduction temperature, $CoFe/SiO_2$ is incompletely reduced. Hence, the effect of reduction temperature should be studied.
3. The $CoCu/SiO_2$ catalyst shows low hydrogenation activity presumably due to low H_2 dissociation activity of copper. Hence, the addition of nickel or palladium to enhance the hydrogenation rate, should be investigated.
4. The low contact time shows high selectivity of C=O bond. Thus, the investigation at low contact time is interesting.

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APPENDIXES

APPENDIX A

REFERENCE X-RAY DIFFRACTION PATTERN OF CATALYST

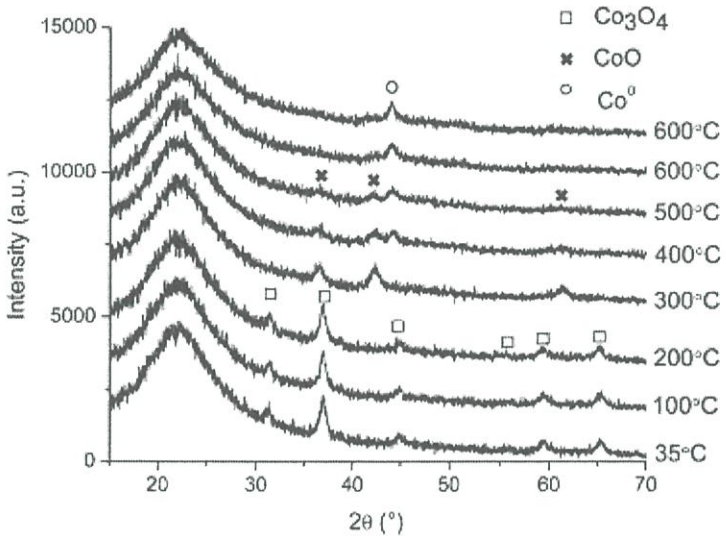

Figure A1 Reference X-ray diffraction pattern of Co/SiO_2 (prepared by incipient wetness impregnation method)[34].

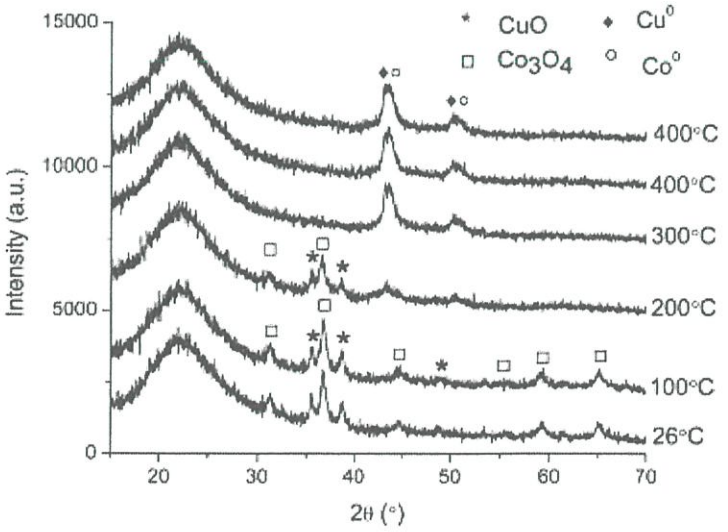

Figure A2 Reference X-ray diffraction pattern of $Co\text{-}Cu/SiO_2$ [34].

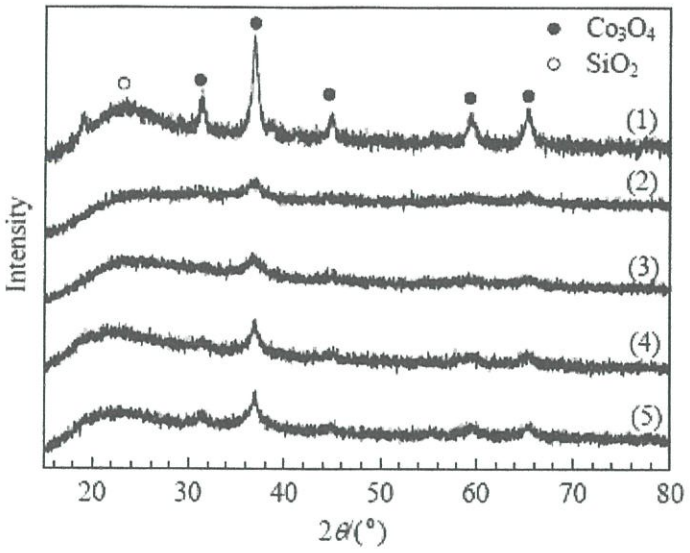

Figure A3 Reference X-ray diffraction pattern of Co-Fe/SiO_2 (4) [33].

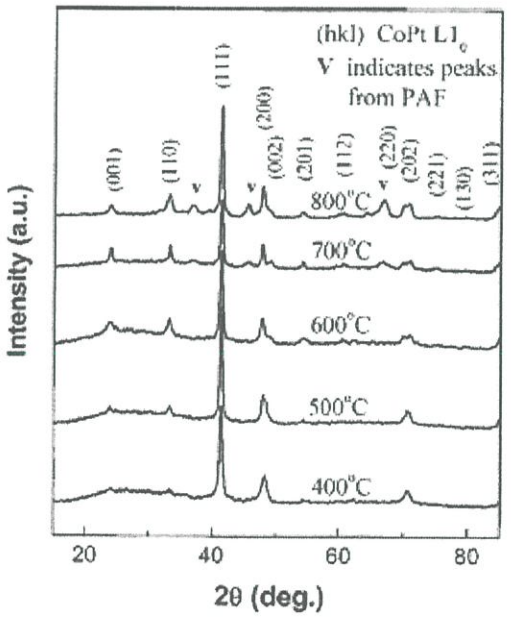

Figure A4 Reference X-ray diffraction pattern of Co-Pt/SiO_2 (nanoparticle) [42].

APPENDIX B

CALCULATION

Calculation of catalytic parameter

Contact time, W/F

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

In the reaction using 0.00068 mol/h of 2-hexenal in feed and using 0.05 grams of catalyst, the W/F is calculated as follow:

$$W/F = [0.05\ (g)/0.00068\ (mol/h)]$$

$$= 73.52\ g.h/mol$$

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 B1 The summation of the peak area for products.

Product	Peak area
Hexanal	87.667
Hexanol	110.228
2-hexenol	166.393
Aldol	146.806
2-hexenal (Feed)	1137.379
Total	1648.473

*In formation of Co-Pt/SiO_2 in cyclohexane, Contact time = 73, time on stream = 300 minutes

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;

$$\%\text{Yield of hexanal} = \frac{87.667 \times 100}{1648.473}$$

$$= 5.3$$

The percent yield of each product obtained from above calculation is shown in **Table B2.**

Table B2 % Yield of product derived by normalization method.

Products	%Yield
Hexanal	5.3
Hexanol	6.7
2-hexenal	10.1
Aldol	8.9
Total	31

Conversion

%Conversion can be calculated from the following equation:

$$\%\text{Conversion} = \frac{\text{Area total - Area feed}}{\text{Area total}}$$

For example;

$$\%\text{Conversion} = \frac{(1648.473 - 1137.379) \times 100}{1648.473}$$

$$= 31.0$$

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;

$$\%\text{Selectivity of 2-hexenal} = \frac{10.1 \times 100}{31}$$

$$= 32.6$$

APPENDIX C

GAS CHROMATOGRAM

Analysis of gas product from gas chromatography

Prior to analysis, the structure of each products in the sample is identified the by GC-MS (gas chromatography with mass spectrometer detector). Then, the quantitative analysis of each products was carried by GC-FID (gas chromatography with flam ionization detector) with the condition expressed in **Table C1**.

Table C1 The GC condition for quantitative analysis

Column	Carbowax, 30 m x 0.32 mm x 0.25 μm
Temperature program	50°C (2 min hold) to 160°C (20 min hold) at 10°C/min
Carrier gas	Nitrogen at 30 ml/min
Injection	50°C
Detector	FID

The chromatogram of gas products were identified using reference standard for comparison in **Table C2**

Table C2 Chromatogram data of standard product distribution and feed

Products or feed	Retention time of standard (min)
Hexanal	3.45
2-hexenal	5.2
Hexanol	7.3
2-hexenol	8.1

APPENDIX D

REACTION DATA

1. Selective hydrogenation of 2-hexenal

1.1 Effect of contact time

Table D1 Product yields after hydrogenation at contact time = 31 g.h/mol

Time on stream (min)	%conversion	%Yield			
		hexanol	aldol	2-hexenol	hexanal
30	26.9	4.8	0	5.2	16.9
60	17.1	1.3	0	4.2	11.6
90	13.0	0.5	0	4.5	8.0
120	11.5	0.4	0.4	4.3	6.4
150	11.9	0.5	1.7	4.2	5.5
180	12.5	0.5	3.4	4.5	4.1
210	12.6	0.4	4.4	4.2	3.6
240	12.2	0.4	4.8	4.2	2.7
270	12.6	0.5	4.8	4.6	2.7
300	12.1	0.4	5.0	4.1	2.6
330	13.3	0.6	5.1	4.7	2.9
360	12.4	0.5	4.4	4.5	3.0

*Reaction condition; Catalyst: Co-Pt/SiO_2, Temperature: 80 °C, Catalyst weight: 0.03 g (diluted in 0.12 g), Carier gas: 30 ml/min of hydrogen, Pressure : 1 atm.

Table D2 Product yields after hydrogenation at contact time = 73 g.h/mol

Time on stream(min)	%conversion	%Yield			
		hexanol	aldol	2-hexenol	hexanal
30	70.4	55.3	0	2.8	12.3
60	52.6	27.2	1.2	10.6	13.6
90	44.2	17.7	2.8	12.2	11.5
120	41.7	14.3	4.5	12.5	10.4
150	36.8	11.8	4.3	11.2	9.5
180	34.0	9.8	5.7	10.2	8.3
210	30.2	7.9	6.2	9.6	6.5
240	30.8	7.4	7.6	9.7	6.1
270	29.4	6.7	7.5	9.5	5.7
300	30.6	6.7	8.3	10.2	5.4
330	29.7	6.5	8.2	9.9	5.1
360	29..	6.3	8.2	9.6	5.0

*Reaction condition; Catalyst: Co-Pt/SiO_2, Temperature: 80 °C, Catalyst weight: 0.05 g (diluted 0.1g silica), Carier gas: 30 ml/min of hydrogen, Pressure : 1 atm.

Table D3 Product yields after hydrogenation at contact time = 185 g.h/mol

Time on stream(min)	%conversion	%Yield			
		hexanol	aldol	2-hexenol	hexanal
30	100.0	100	0	0	0
60	99.0	98.0	0	0	1.0
90	95.2	85.1	0.3	3.5	6.3
120	83.9	64.5	0.4	6.9	12.1
150	73.5	45.9	0.3	12.9	14.4
180	65.0	34.6	0	14.9	15.5
210	64.8	32.9	0.4	15.5	16.0
240	57.9	27.6	0	15.2	15.1
270	56.2	25.1	0.4	16.3	14.4
300	55.8	24.9	0.4	15.9	14.6
330	54.3	23.4	0.5	16.5	13.9
360	51.2	20.2	0.8	16.3	13.9

*Reaction condition; Catalyst: Co-Pt/SiO_2, Temperature: 80 °C, Catalyst weight: 0.05 g (diluted 0.1g silica), Carier gas: 30 ml/min of hydrogen, Pressure : 1 atm.

Table D4 Product yields after hydrogenation at contact time = 369 g.h/mol

Time on stream(min)	%conversion	%Yield			
		hexanol	aldol	2-hexenol	hexanal
30	100	100	0	0	0
60	100	98.9	1.1	0	0
90	97.3	95.4	0.9	0	1.0
120	95.2	91.6	0.9	0	2.7
150	92.9	84.7	0.8	0	7.4
180	88.7	71.8	1.2	6.7	9.0
210	85.0	63.7	0.9	8.5	11.9
240	81.8	54.7	1.0	12.7	13.4
270	79.0	48.9	1.3	14.7	14.1
300	75.3	43.2	1.2	15.6	15.3
330	71.6	35.7	1.8	17.8	16.3
360	72.6	34.8	2.3	18.5	17.0

*Reaction condition; Catalyst: Co-Pt/SiO_2, Temperature: 80 °C, Catalyst weight: 0.05 g (diluted 0.1g silica), Carier gas: 30 ml/min of hydrogen, Pressure : 1 atm.

1.2 Effect of different metal loded

Table D5 Product yields after hydrogenation over Co/SiO_2 in cyclohexane solvent

Time on stream(min)	%conversion	%Yield			
		hexanol	aldol	2-hexenol	hexanal
30	57.1	39.6	0	5.2	12.3
60	33.2	12.5	0	8.7	12.0
90	27.9	9.0	0	8.3	10.6
120	25.5	7.8	0	8.7	9.0
150	23.6	6.7	0	8.4	8.5
180	21.2	6.1	0	7.6	7.6
210	20.8	5.2	1.6	7.1	6.8
240	21.4	5.1	2.6	7.5	6.1
270	20.8	4.4	3.3	7.1	6.0
300	20.2	4.1	4.4	7.2	4.5
330	21.3	4.0	6.0	7.2	4.2
360	22.3	3.7	7.5	7.4	3.7

*Reaction condition; Contact time: 73, Temperature: 80 °C, Catalyst weight: 0.05 g (diluted 0.1 g silica), Carier gas: 30 ml/min of hydrogen, Pressure : 1 atm.

Table D6 Product yields after hydrogenation over Co-Pt/SiO_2 in cyclohexane solvent

Time on stream(min)	%conversion	%Yield			
		hexanol	aldol	2-hexenol	hexanal
30	70.4	55.3	0	2.8	12.3
60	52.6	27.2	1.2	10.6	13.6
90	44.2	17.7	2.8	12.2	11.5
120	41.7	14.3	4.5	12.5	10.4
150	36.8	11.8	4.3	11.2	9.5
180	34.0	9.8	5.7	10.2	8.3
210	30.2	7.9	6.2	9.6	6.5
240	30.8	7.4	7.6	9.7	6.1
270	29.4	6.7	7.5	9.5	5.7
300	30.6	6.7	8.3	10.2	5.4
330	29.7	6.5	8.2	9.9	5.1
360	29.1	6.3	8.2	9.6	5.0

*Reaction condition; Contact time: 73, Temperature: 80 °C, Catalyst weight: 0.05 g (diluted 0.1 g silica), Carier gas: 30 ml/min of hydrogen, Pressure : 1 atm.

Table D7 Product yields after hydrogenation over Co-Fe/SiO_2 in cyclohexane solvent

Time on stream(min)	%conversion	%Yield			
		hexanol	aldol	2-hexenol	hexanal
30	28.2	14.8	0	3.3	10.1
60	16.6	7.2	0	4.0	5.4
90	7.9	2.8	0	1.8	3.3
120	4.4	1.5	0	0.8	2.1
150	3.9	1.3	0	0.7	1.9
180	7.1	1.0	3.1	1.1	1.9
210	9.5	0.8	6.2	1.0	1.5
240	13.4	0.5	10.5	1.3	1.1
270	19.1	0.6	15.9	1.5	1.1
300	21.0	0.5	18.1	1.4	1.0
330	22.2	0.5	19.2	1.4	1.1
360	22.1	0.5	19.0	1.5	1.1

*Reaction condition; Contact time: 73, Temperature: 80 °C, Catalyst weight: 0.05 g (diluted 0.1 g silica), Carier gas: 30 ml/min of hydrogen, Pressure : 1 atm.

Table D8 Product yields after hydrogenation over Co-Cu/SiO_2 in cyclohexane solvent

Time on stream(min)	%conversion	%Yield			
		hexanol	aldol	2-hexenol	hexanal
30	24.9	5.3	0	2.2	17.4
60	17.2	1.7	1.0	2.5	12.0
90	13.0	0.6	0.9	2.1	9.4
120	7.4	0	0.8	1.1	5.5
150	5.6	0	0.9	0.9	3.8
180	5.1	0	1.2	0.8	3.1
210	9.2	0	5.5	1.3	2.4
240	9.3	0	6.3	1.1	2.5
270	12.2	0	8.6	1.3	2.3
300	17.6	0	14.1	1.4	2.1
330	20.3	0	16.6	1.4	2.3
360	21.2	0.4	16.8	1.8	2.2

*Reaction condition; Contact time: 73, Temperature: 80 °C, Catalyst weight: 0.05 g (diluted 0.1 g silica), Carier gas: 30 ml/min of hydrogen, Pressure : 1 atm.

1.3 Compare product selectivity of Co/SiO_2 and $CoPt/SiO_2$

Table D9 Product yield after hydrogenation over Co/SiO_2 at contact time 73 g.h/mol feed

Time on stream(min)	%conversion	%selectivity	Yield			
			hexanal	hexanol	2-hexenol	aldol
30	57.1	9.1	12.3	39.6	5.2	0
60	33.2	26.2	12.0	12.6	8.7	0
90	27.9	29.9	10.6	9.0	8.3	0
120	25.5	34.1	9.0	7.8	8.7	0
150	23.6	35.4	8.5	6.7	8.4	0
180	21.2	35.6	7.6	6.1	7.6	0
210	20.8	34.2	6.8	5.2	7.1	1.6
240	21.4	35.2	6.1	5.1	7.5	2.6
270	20.7	34.1	6.0	4.4	7.1	3.3
300	20.3	34.2	4.6	4.3	6.9	4.5
330	21.3	33.7	4.2	4.0	7.2	6.0
360	22.3	33.3	3.7	3.7	7.4	7.5

*Reaction condition; Solvent: cyclohexane, Reaction temperature: 80°C, Carier gas: 30 ml/min of hydrogen, Catalyst weight : 0.05 g(diluted 0.1 g silica), Pressure : 1 atm.

Table D10 Product yields after hydrogenation over $CoPt/SiO_2$ at contact time 52 g.h/mol feed

Time on stream(min)	%conversion	%selectivity	Yield			
			hexanal	hexanol	2-hexenol	aldol
30	36.1	31.9	8.7	15.0	11.5	0.9
60	25.8	45.4	5.0	7.5	11.7	1.6
90	22.8	47.4	4.4	5.6	10.8	2.0
120	21.5	44.7	5.2	4.2	9.6	2.5
150	21.0	42.1	5.2	3.6	8.9	3.3
180	21.1	41.0	4.9	3.4	8.6	4.1
210	18.9	37.6	4.5	3.4	7.1	3.9
240	18.2	38.1	3.9	2.9	6.9	4.4
270	17.8	38.0	3.5	2.6	6.7	4.9
300	17.6	38.9	3.1	2.4	6.8	5.2
330	17.3	39.9	3.0	2.1	6.9	5.4
360	18.1	38.2	3.4	2.1	6.9	5.6

*Reaction condition; Solvent: cyclohexane, Reaction temperature: 80°C, Carier gas: 30 ml/min of hydrogen, Catalyst weight : 0.05 g(diluted 0.1 g silica), Pressure : 1 atm.

Table D11 Product yields after hydrogenation over $CoPt/SiO_2$ at contact time 60 g.h/mol feed

Time on stream (min)	%conversion	%selectivity	Yield			
			hexanal	hexanol	2-hexenol	aldol
30	54.3	29.0	6.9	31.7	15.7	0
60	36.8	38.8	8.0	14.5	14.3	0
90	32.7	45.5	7.3	10.5	14.9	0
120	30.6	40.4	9.3	8.9	2.4	0
150	31.2	47.2	7.7	8.4	14.7	0.4
180	30.4	46.1	7.8	7.7	14.0	0.9
210	26.7	46.2	7.0	6.4	12.3	0.9
240	28.1	42.9	7.9	5.5	12.1	2.6
270	27.2	42.5	7.4	5.4	11.6	2.9
300	29.7	44.5	7.0	5.8	13.3	3.6
330	27.6	45.9	5.7	5.2	12.8	4.1
360	26.3	48.2	5.7	6.0	12.6	1.9

*Reaction condition; Solvent: cyclohexane, Reaction temperature: 80°C, Carier gas: 30 ml/min of hydrogen, Catalyst weight : 0.05 g(diluted 0.1 g silica), Pressure : 1 atm.

1.4 Effect of solvent over Co-Pt/SiO_2 catalyst

Table D12 Product yields after hydrogenation over Co-Pt/SiO_2 in methanol solvent

Time on stream(min)	%conversion	%Yield			
		hexanol	isomer	2-hexenol	hexanal
30	98.1	1.6	60.9	0	35.6
60	82.6	1.5	55.4	0	25.7
90	65.4	0.8	39.4	0	25.2
120	59.6	0.6	33.8	0.3	24.9
150	55.2	0.4	31.6	0.3	22.9
180	54.5	0.4	28.0	0.3	25.8
210	54.2	0.3	27.6	0	26.3
240	54.0	0.5	29.2	0	24.3
270	51.4	0.3	26.4	0.2	24.5
300	50.6	0.3	25.7	0	24.6
330	48.9	0.4	26.2	0	22.3
360	49.6	0.5	25.7	0	23.4

*Reaction condition; Contact time: 73, Temperature: 80 °C, Catalyst weight: 0.05 g (diluted 0.1 g silica), Carier gas: 30 ml/min of hydrogen, Pressure : 1 atm.

Table D13 Product yields after hydrogenation over Co-Pt/SiO_2 in cyclohexane solvent

Time on stream(min)	%conversion	%Yield			
		hexanol	aldol	2-hexenol	hexanal
30	70.4	55.3	0	2.8	12.3
60	52.6	27.2	1.2	10.6	13.6
90	44.2	17.7	2.8	12.2	11.5
120	41.7	14.3	4.5	12.5	10.4
150	36.8	11.8	4.3	11.2	9.5
180	34.0	9.8	5.7	10.2	8.3
210	30.2	7.9	6.2	9.6	6.5
240	30.8	7.4	7.6	9.7	6.1
270	29.4	6.7	7.5	9.5	5.7
300	30.6	6.7	8.3	10.2	5.4
330	29.7	6.5	8.2	9.9	5.1
360	29.1	6.3	8.2	9.6	5.0

*Reaction condition; Contact time: 73, Temperature: 80 °C, Catalyst weight: 0.05 g (diluted 0.1 g silica), Carier gas: 30 ml/min of hydrogen, Pressure : 1 atm.

1.5 Effect of reaction temperature (liquid & gas phase) over Co-Pt/SiO_2 catalyst

Table D14 Product yields after hydrogenation at 80°C

Time on stream(min)	%conversion	%Yield			
		hexanol	isomer feed	2-hexenol	hexanal
30	98.1	1.6	60.9	0	35.6
60	82.6	1.5	55.4	0	25.7
90	65.4	0.8	39.4	0	25.2
120	59.6	0.6	33.8	0.3	24.9
150	55.2	0.4	31.6	0.3	22.9
180	54.5	0.4	28.0	0.3	25.8
210	54.2	0.3	27.6	0	26.3
240	54.0	0.5	29.2	0	24.3
270	51.4	0.3	26.4	0.2	24.5
300	50.6	0.3	25.7	0	24.6
330	48.2	0.4	26.2	0	22.3
360	49.6	0.5	25.7	0	23.4

*Reaction condition; Catalyst: Co-Pt/SiO_2, Solvent: Methanol, Catalyst weight: 0.05 g (diluted 0.1 g silica), Carier gas: 30 ml/min of hydrogen, Pressure : 1 atm.

Table D15 Product yields after hydrogenation at 120°C

Time on stream(min)	%conversion	%Yield			
		hexanol	isomer feed	2-hexenol	hexanal
30	78.5	56.3	4.7	1.3	16.2
60	68.2	27.3	7.7	1.2	32.0
90	64.3	18.5	9.3	1.6	34.9
120	57.2	6.8	11.8	1.1	37.5
150	58.9	4.7	13.0	0.6	40.6
180	57.7	3.3	13.1	0.3	40.9
210	54.6	1.5	14.1	0.3	38.7
240	50.3	1.4	13.7	0.2	35.0
270	51.3	0.6	14.6	0.3	35.8
300	49.0	0.5	14.6	0.2	33.8
330	45.5	0.3	14.0	0.3	30.9
360	46.1	0.2	14.8	0.3	30.8

*Reaction condition; Catalyst: Co-Pt/SiO_2, Solvent: Methanol, Catalyst weight: 0.05 g (diluted 0.1 g silica), Carier gas: 30 ml/min of hydrogen, Pressure : 1 atm.