การเปลี่ยนอะซิทอลเป็น 1-โพรพานอล ด้วยปฏิกิริยาไฮโดรดีออกซิจิเนชัน โดยใช้ตัวเร่งปฏิกิริยา Ni-Cu/H-ZSM 5 และ Ni-Cu/Al_2O_3

HYDRODEOXYGENATION OF ACETOL TO 1-PROPANOL OVER Ni-Cu/H-ZSM 5 AND Ni-Cu/Al_2O_3 CATALYSTS

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โครงงานพิเศษนี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรวิทยาศาสตรบัณฑิต
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JETSADAH PREMPREE

MONRUETHAI FUNGMONGKONSATHIAN

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Abstract

Ni-Cu supported H-ZSM-5 and Al_2O_3 catalysts were prepared by wetness impregnation method and tested of the acetol hydrodeoxygenation to 1-propanol under ambient H_2 pressure. XRF shows that the Ni and Cu loading in the catalysts (~3% and ~4%, respectively) are higher than the expected value. TPR exhibits that the Ni-Cu alloy of Ni-Cu/H-ZSM-5 catalyst is higher than that of the Ni-Cu/Al_2O_3 catalyst. The excess Ni metal is separately dispersed on the H-ZSM-5 while Cu metal is separately occluded on the Al_2O_3 support. N_2-Physisorption shows that the Ni-Cu/H-ZSM-5 catalyst (240 m^2/g) has higher surface area, as compared with Ni-Cu/Al_2O_3 catalyst (109 m^2/g). NH_3-TPD shows that the acidity of Ni-Cu/H-ZSM-5 catalyst is higher than that of Ni-Cu/Al_2O_3 catalyst. Acetol can be hydrogenated to 1,2-propanediol followed by dehydration to propanaldehyde or acetone and rapidly hydrogenation to 1-propanol or 2-propanol, respectively. The Ni-Cu/H-ZSM-5 catalyst is more active than the Ni-Cu/Al_2O_3 catalyst. This is because the dehydration function of the two catalysts is different. The Ni-Cu/H-ZSM-5 catalyst possesses Bronsted acid and selectively produced 1-propanol while the Ni-Cu/Al_2O_3 catalyst contains Lewis acid sites that selectively give 2-propanol. Moreover, the conversion of acetol and the yield of 1-propanol increased with an increase in the reaction temperature for the Ni-Cu/H-ZSM-5 catalyst. But, the catalyst is rapidly deactivated due to formation of high molecular weight by aldol condensation. The study performed with the optimized catalyst revealed that the acetol can be adsorbed on the metal sites of the catalyst and hydrogenated to 1,2-propanediol. Such intermediate is then dehydrated to propanaldehyde that is hydrogenated presumably by hydrogen spilled over to form 1-propanol. The Ni-Cu/H-ZSM-5 catalyst promotes acetol conversion and 1-propanol selectivity higher than the Ni-Cu/ Al_2O_3 catalyst at 200 °C.

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Jetsadah Prempree

Monruethai Fungmongkonsathian

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Glycerol is a valuable by-product from biodiesel production via trans-esterification of triglyceride [1]. Glycerol is widely used as raw materials for production of higher valued chemicals such as 1,3-propanediol, acrolein and related acrylate monomer [2]. For the dehydration of glycerol to acrolein over acid catalyst, various by-products were obtained. One of the major by-product is acetol (hydroxyacetone) formed in a paralleled dehydration at primary OH group [3]. Acetol is an oxygenated compound that is not useful and relatively unstable. This compound tends to decompose at high temperature or condense to higher molecular weight product leading to coke formation. Therefore it is interesting to convert acetol to others high valued compound such as n-propanol and 1,2-propanediol [4].

Acetol can be converted to n-propanol by hydrodeoxygenation via hydrogenation to 1,2-propanediol followed by dehydration to propanaldehyde and hydrogenation to n-propanol. The hydrogenation can be promoted by metal catalysts, such as copper, platinum, nickel while the dehydration can be catalyzed by acidic support, such as alumina and zeolites [5,6]. Copper was added to nickel catalysts as promoter because it can decrease chance to decarbonylation and hydrogenolysis that may take place in the reaction [7,8]. Moreover, Ni is typically used as the catalyst for hydrogenation because it is relatively cheaper, as compared to Pt or Pd. In hydrodeoxygenation, Ni-Cu catalyst is suitable for this reaction because of strong interaction with carbonyl group of acetol and propanaldehyde. In addition, acidic catalyst like alumina and H-ZSM-5 has high surface area and high thermal stability with strong interaction with 1,2-propanediol, a product from acetol hydrogenation. Dehydration of 1,2-propanediol can be readily promoted to form propanaldehyde that is hydrogenated to n-propanol. Hence bi-functional catalyst is appropriate choice for the hydrodeoxygenation of acetol to n-propanol. However, hydrogenation is exothermic and takes place at low temperature under hydrogen pressure while dehydration is endothermic and preferred at high temperature, therefore the reaction temperature will be optimized to facilitate both reactions in this work. Moreover, the effect of contact time and type of support on hydrogenation activity will be investigated.

1.2 Objectives

1. To obtain metal-acid bi-functional catalyst for acetol hydrodeoxygenation.
2. To investigate the effect of metal and type of supports.
3. To study the reaction temperature, contact time and deactivation of the catalysts.

1.3 Scopes of study

The scopes of this thesis are as follows:

1. Catalyst preparation by wetness impregnation of copper and nickel on suitable support that is alumina and zeolites H-ZSM-5.
2. Characterization of catalyst by X-ray Fluorescence (XRF), Temperature-programmed reduction (TPR), Temperature programmed desorption (TPD) and Gas adsorption analysis (BET).
3. Study on thermal factor that effect the reaction.
4. Study on hydrodeoxygenation of acetol with various catalysts in a continuous fixed-bed reactor.
5. Analysis and quantification of liquid products by Gas chromatography with flame ionization detector (GC-FID).

1.4 Expected results

It is expected that a new technology for production of n-propanol from acetol will be obtained. This technology could potentially be developed into a process for n-propanol production from by-production of glycerol.

CHAPTER 2

LITERATURE REVIEWS AND THEORY

2.1 Acetol

Acetol is a ketone compound which is also known as hydroxyacetone. Its IUPAC name is 1-hydroxy-2-propanone. Acetol is extremely reactive as it contains both hydroxyl and carbonyl functional groups. It is hygroscopic and miscible with ethanol and ethyl ether. The first synthesis of acetol has been made by reacting bromoacetone and sodium or potassium formate or acetate, followed by hydrolysis of the ester by methyl alcohol. Treatment of glycerol or propylene glycol at 200 °C to 300 °C with a dehydrogenating catalyst leads to the formation of acetol, while the direct oxidation of acetone with Bayer and Villager's acetone-peroxide reagent produces acetol together with pyruvic acid.

Reportedly, acetol plays a role as an organic synthesis intermediates or starting materials. It is widely used in the industries as the structure of acetol itself can promote variety of reaction including dehydration, hydrogenation, oxidation and polymerization. Acetol is mainly used to produce products such as propylene glycol via hydrogenation reaction and acrolein through dehydration. It is also used to synthesize compounds such as propanaldehyde, acetone and furan derivatives.

In food industry, acetol has been extensively used to give aroma to foods. It gives strong odor to the bread which is almost identical to proline, valine and isouleucine i.e. constituents that are frequently used as bread flavors. Moreover, it is also used to induce flavor compounds in heated milk. The taste of acetol is characterized by many descriptors depending upon the medium. In aqueous solutions, acetol is described as sweet and roasted. In contrast, acetol is described as yogurt-like in emulsions. Acetol is formed as the product of carbohydrate fragmentation or degradation that occurs during non-enzymatic browning reactions or known as the Maiilard Reaction.

Meanwhile in textile industry, acetol can be used as a substitute to sodium dithionite which is usually used to reduce dye to a water soluble compound. Usually in textile industry, vat dyes are used to give color as it is water insoluble and generally based around anthriquinone or indigo. As the dyes displayed excellent color fastness and UV stability, they are often used for fabrics that must withstand frequent, harsh washing such as military uniforms and hospital textiles or those continuously exposed to daylight such as furnishings. However, as the dyes are water insoluble, redox chemistry need to be employed to allow fixation in which the dye stuff is initially reduced to a water soluble compound using sodium dithionite, but this results in sulphur salts in the waste. In order to overcome this problem, acetol can be used as a substitute, though there is some limitation as it can only reduce some of the dyes.

Apart from that, acetol is also used as main constituent of skin tanning agent in cosmetic industry as well as to provide expedient access to both natural carbohydrates and unnatural polyhydroxylated molecules of significance in medicine. For a long time, the direct catalytic asymmetric aldol reaction of a-hydroxylated ketones with aldehydes had only been achieved with protein catalysts such as aldolases and catalytic antibodies.

2.1.1 Conversion of glycerol to acetol

The production of acetol from glycerol is greatly influenced by the presence of catalyst. The most famous catalyst used in the production of acetol from glycerol is the metal supported acidic catalyst. This phenomenon may be due to the acidic catalysts favour the elimination reaction while the transition metal catalyst involves in promoting the carbonylation reaction. Based on a research reported, acetol can be yielded in the presence of moderate acidic support catalyst, **Fig. 2.1**. In their preliminary work, several tests were performed with selected catalysts at 280°C by using fixed-bed reactor. Pure alumina and titania supports with low acidity showed a very low conversion of glycerol (10–15%) at 280°C. In contrast, the used of strong acidic support catalyst decreases the conversion of acetol and increases the yield of acrolein. They compared the catalysts reactivity of Al_2O_3 and TiO_2 supports by PO_4^- ions, Silico-Alumino-Phosphate-11 (SAPO) and SAPO-34. Based on the results, the optimum catalyst was found to be SAPO-11 with 70% glycerol conversion and 65% acetol selectivity; while the least reactive catalyst was the SAPO-34 with 50% glycerol conversion and 50% acetol selectivity. Kinage *et al.* (2010), studied the production of acetol from glycerol using a continuous fixed-bed reactor with the presence of sodium-doped metal oxide catalysts. The selected metal oxide catalysts which are CeO_2, Al_2O_3, ZrO_2 and Ga_2O_3 were doped with 5% wt. of sodium. They found that the formation of acetol from glycerol need moderate acid-base site of catalyst. Catalyst with high basic site will leads to produce allyl alcohol, while excess basic site gives further cracking of acetol and forms ethylene glycol as by-product. The results showed that the Na-doped CeO_2 gave highest selectivity of acetol (68.6%) followed by Na/Al_2O_3 (57.3%), Na/ZrO_2 (49.8%) and Na/Ga_2O_3 (35.2%).

A study by Chiu *et al.* (2006) has been carried out using reactive distillation operated in batch and semi batch mode with the presence of copper-chromite catalyst. In their preliminary catalyst screening, they found that copper-chromite catalyst showed superior acetol selectivity compared to Ru, Pt, Pd and Ni catalysts. 90% acetol selectivity was achieved over copper-chromite catalyst at 240°C and 98 kPa. It is known that copper-chromite catalyst exhibits poor hydrogenolytic activity toward C-C bonds and efficient activity for C-O bond hydro-dehydrogenation. They continued their study by batch and semi-batch mode in order to obtain the optimum production of acetol and found that semi-batch mode increases glycerol conversion (92.71%) and acetol selectivity (90.62%). They concluded that catalytic conversion of glycerol to acetol via semi-batch reactive distillation exhibits higher yield, higher selectivity and lower-residue formation than batch due to the semi-batch operation has a higher catalyst loading to glycerol ratio in the reaction. However, they did not clarify the active species of copper although chromium seems to be the active species. In another work, the same catalyst was also used in their new approaches using vapor-phase and liquid-phase packed bed reactor. The vapor-phase packed bed reaction carried out in a stainless steel tube and the reactor packed with pellets of copper-chromite catalyst. The study showed that vapor-phase packed bed reaction has higher glycerol conversion (22.1%) and higher acetol selectivity (61.99%) than liquid-phase packed bed reaction with 20.4% glycerol conversion and 29.90% acetol selectivity. They clarified that the residence time for the gas is much less than for the liquid. The density of the acetol is lower in the gas phase which dramatically reduces polymerization reactions that contributed to higher order reaction.

The conversion of glycerol to acetol can be also obtained without using acidic supported catalyst. This research has been done by Yamaguchi *et al.* (2010), using high-temperature liquid water in the presence of carbon dioxide at 300 °C. In the absent of carbon dioxide, the conversion of glycerol is reported to be as low as 40% with 0.5% acetol selectivity. The glycerol conversion increases from 40 to 50% by the addition of carbon dioxide and the acetol yield also increases from 0.5 to 1% at 1.5 hours by the addition of carbon dioxide. This indicates that carbon dioxide enhanced the yields of the solid substance and acetol. The increase in acetol yield can be explained by the increased in acidity of the solvent. This is due to the formation of carbonic acid when the carbon dioxide is dissolved in the high-temperature liquid water.

2.1.2 Acetol from other resources

Acetol can be also synthesized from propylene glycol via dehydrogenation process. However, this type of reaction is less popular reaction due to the minimal economic viability of the process. In prior work, Disselkamp *et al.* (2008) used aqueous propylene glycol and hydrogen peroxide with the presence of Pd-black catalyst under reflux conditions at 95 °C to synthesize acetol. Unfortunately, acetic acid was also found to be the second major products apart from a lesser abundant compound formed which was the lactic acid. From the study, it is seen that the yield of acetol is 38% and does not vary greatly with increasing addition of H_2O_2. It is proved that at 5 equivalents H_2O_2 a 65% conversion exists and acetol:acetic acid ratio of 2:1 is seen. The experiments also revealed that although the product distribution in chemistries is similar, the amount of reactive oxygen is greatly enhanced with co-addition of O_2/H_2O.

Research by Sato *et al.* (2008) showed that the dehydrogenation of 1,2-propanediol with the presence of Cu-Al_2O_3 catalyst at 250°C can be carried out using vapor-phase reaction. In this process, alcohols are dehydrogenated to form corresponding carbonyl compounds and copper is used as it is a well-known dehydrogenation catalyst. The dehydrogenation of 1,2-Propanediol has resulted in a 60.8% conversion and 71.3% acetol selectivity with a small amount of acetone (5.2%) and propanoic acid (2.2%) generated as by products.

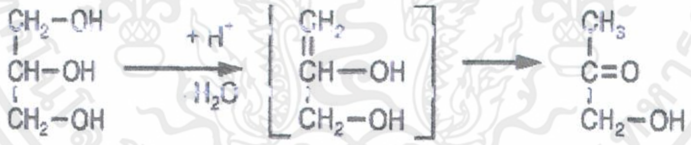


Figure 2.1 Schematic for the dehydration of glycerol to acetol suggested by Suprun *et al.* (2009).

From the prior research reported, acetol can be produce from C6 sugar such as glucose, sucrose and sorbitol. The synthesis of acetol from sugar using reactive distillation technique has been studied by Dasari (2006). In his study, the used of nickel-based catalyst has converted sorbitol to lower polyols with the selectivity of C3 derivatives to be more than 80%. The C3 derivative consists of propylene glycol, glycerol and acetol. However, he did not state the selectivity of the products obtained. The reaction was performed at 230 °C and 250 psi hydrogen pressure for 12 hours with the presence of 5% catalyst. The conversions of glucose and sucrose are nearly as effective as the use of sorbitol. Glycerol dissolves and stabilizes sorbitol in a manner much like water which consequently allows the reactions to be conducted without the presence of water. The preliminary results of the study illustrate that high selectivity for conversions of C6 feedstock can be maintained even at lower water contents. The yield remained high where up to 75% sugar was found to be present in the water. This indicates a more effective use of reactor volumes at 75% sugar relative to 25% sugar. These findings have created opportunities to use reactive distillation for sorbitol conversion to achieve higher yields.

In earlier work by Yan *et al.* (2008), they described that acetol can be obtained from C6 sugar (sorbitol) under batch mode gas phase heterogeneous. They identified copper chromite as effective catalyst than palladium catalyst. The optimum conditions of the hydrogenolysis were at 290 °C and 0.3 bar with 2.5% sorbitol aqueous feed. These conditions yielded a 25% acetol. The by-products such as acetone and 1-hydroxy-2-butanone were also formed in this process.

2.1.3 Industrial producer of acetol

United States is the major producer country of acetol since the technology was discovered by a group of local researchers in 2006. However, they exploited it as a building block to produce propylene glycol. The Senergy Chemical from U.S claims that the propylene glycol can be produced under novel conditions which are low temperature and low pressure. In this process, glycerol is initially catalytically converted into acetol and subsequently hydrogenated into propylene glycol. The process is efficient, as it produces small to negligible amount of waste and it only generates a non-toxic chemical derived from a natural material. Senergy Chemical is a global license holder of this technology. The technology converting glycerol to propylene glycol was developed by Suppes and Sutterlin at the University of Missouri in United States. In this technology, hydrogen is used as a co-reagent to perform a hydrogenolysis conversion of glycerine, in the presence of a copper-chromite catalyst. Initially, water molecules are removed from the glycerine and this process is then followed by the addition of hydrogen molecules. This process yields two products which are acetol and propylene glycol as well as some water as by-product. According to Suppes, the formation of ethylene glycol in this process is undesirable because of its toxicity as well as every pound of ethylene glycol produced has resulted in the formation of another 0.5 pound of unwanted by-products [9].

2.2 Porous materials

Classically porous materials are organic materials, polymeric foams. A large number of inorganic porous materials have been developed, e.g. for insulation, cushioning, impact protection, catalysis, membranes, construction materials.

2.2.1 Porosity

Porous means contain pores (cavities, channels, interstices) which are deeper than they are wide either describe the pores, or describe the cell/pore walls.

Accessibility:	**Shape:**
a: Closed pores	c: Cylindrical open
b,c,d,e,f: Open pores	f: Cylindrical blind
b, f: Blind pores (dead-end or saccate)	b: Ink-bottle-shaped
e: Through pores	d: Funnel shaped
c: Cylindrical open	g: Roughness

Figure 2.2 Different types of pores.

Table 2.1 Definition of terms used to characterize porous solids.

Density	true density	density of a material excluding pores and interparticle voids (density of the solid network)
	apparent density	density of a material including closed and inaccessible pores
	bulk density	density of the material including pores and interparticle voids (mass per total volume, with volume = solid phase + closed pores + open pores)
Pore volume	V_p	volume of the pores
Pore size		also called pore width (diameter): the distance of two opposite walls of the pore
Porosity		ratio of the total pore volume V_p to the apparent volume V of the particle or powder
Surface area		the accessible (or detectable) area of solid surface per unit mass of material

2.2.2 Measuring porosity

The measured value depends on the method. Some detects only open pores, e.g. adsorption of molecules (Open pore and accessibility is then defined by the probe molecule). Other may probe also closed pores, e.g. spectroscopy, diffraction, and scattering.

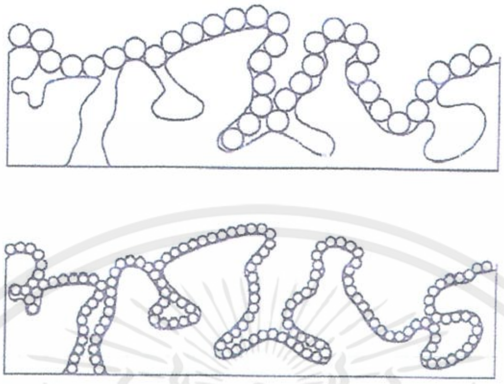


Figure 2.3 Schematic of gas adsorption on a porous material by gases of different molecular size.

The surface area, when measured with large molecules, is smaller than when smaller molecules are used.

2.2.3 Pore size

Pore size is important for catalytic applications. IUPAC has classified three pore size regimes, associated with transport mechanisms:

- ***Microporous***, smaller than 2 nm
- ***Mesoporous***, between 2 and 50 nm
- ***Macroporous***, larger than 50 nm

Macropores : larger than typical mean free path length of typical fluid. Bulk diffusion and viscous flow.

Mesopores : same order or smaller than the mean free path length. Knudsen diffusion and surface diffusion. Multilayer adsorption and capillary condensation

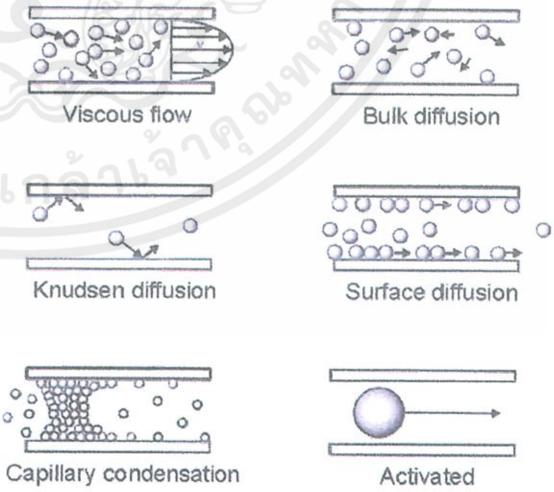


Figure 2.4 Transport mechanisms through pores.

Micropores : pore size comparable to the molecules. Activated transport dominates.

2.2.4 Microporous crystalline solids: Zeolites

Zeolites are porous, hydrated aluminosilicates. They may be natural minerals or synthetic materials.

The general chemical composition of a zeolite is:

$M^{n}_{x/n}Si_{1-x}Al_xO_2 \cdot yH_2O$

Where M = e.g. Na^{+}, K^{+}, Li^{+}, Ag^{+}, NH^{4+}, H^{+}, Ca^{2+}, Ba^{2+}

Characteristics of zeolites:

1) Tectosilicates, i.e. three dimensional structure built from tetrahedra. Some silicon atoms have been replaced by aluminium, i.e. the (Si+Al)/O = ½. (Tetrahedra usually denoted T-atoms.)

2) Open framework structure built from TO_4-tetrahedra, containing pores and voids. The structure and porosity are periodic (i.e. crystalline materials). The pore shaves molecular dimensions.

3) Counter ions (cations) are presented in order to compensate the negative framework charge created by aluminium substitution. The counter ions are situated in the pores and voids, and are usually mobile.

4) In the voids and pores are also water molecules (zeolitic water). One measure of the porosity is the amount of adsorbed water. The water molecules are also presented in the pores and voids, and may (in many cases) be removed by heating and readsorbed at lower temperatures.

5) Loewensteins rule imposes a limit to the amount of aluminium which may be substituted into the framework: No Al-O-Al may be present in tectosilicates. This means that only half of the silicon atoms may be substituted by aluminium. For the general composition:

$$M^{n}_{x/n}Si_{1-x}Al_xO_2 \cdot yH_2O$$

This means that the Si/Al ratio is larger than 1 and that x is smaller than 0.5. This rule is not always obeyed! (High aluminium e.g. Si/Al = 0.5). High silica and pure silica zeolites have been synthesized

2.2.4.1 Catalysis: Zeolites

One of the major uses of zeolites is as heterogeneous catalysts in the petrochemical industry. Cracking catalysts (H-form of zeolite Y, faujasite) is the largest use of zeolites. They are used also for production of synthetic gasoline (ZSM-5) from methanol and synthesis of fine chemicals. Zeolite catalysts give high selectivity (shape selective) and their properties may be tailored by changing the chemistry, e.g. Si/Al ratio and counter cations.

2.2.4.2 Zeolite synthesis

The first laboratory study the synthesis of a zeolite is attributed to Deville, who in 1862 synthesized levyne (levynite) $Ca_9\ [Al_{18}Si_{36}O_{108}]\ .50\ H_2O$ by heating potassium silicate and sodium aluminate in a glass ampoule. A large increase in synthesis of zeolites was seen after 1940 when X-ray diffraction became a common tool for analysis.

Zeolites are usually synthesized from a basic medium (sol or gel) under mild to medium hard hydrothermal conditions (70-350 °C). They mainly obtained as powder as very small crystals. The important components for zeolite synthesis are: water, silica source, alumina source, pH-regulators, and templates (catalysts, nucleation centers).

Parameters have to be considered during zeolite synthesis:

- Composition
- Temperature
- pH
- Temperature ramps
- Ageing conditions
- Stirring rate
- Order of mixing

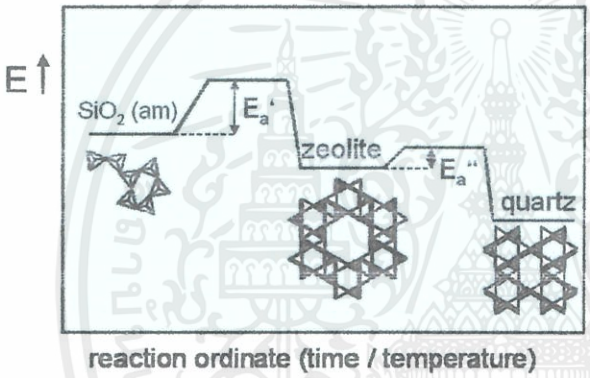


Figure 2.5 Activation energy and reaction ordinate of zeolite synthesis.

Zeolite synthesis is still mainly done by trial and error with some knowledge and experience.

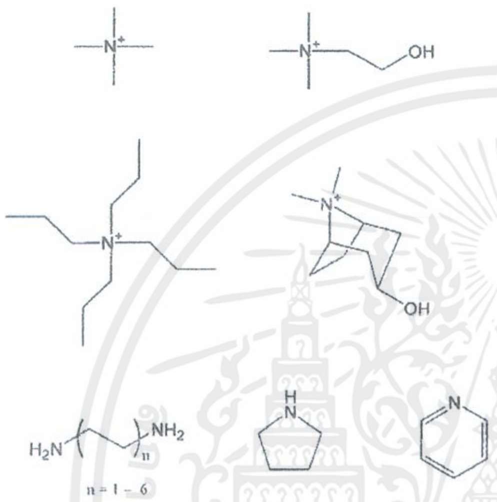
Table 2.2 Influence of different components of the reaction mixture on the zeolite structure.

Reaction mixture composition	Primary influence
SiO_2/Al_2O_3 ratio	framework composition
H_2O/SiO_2 ratio	rate; crystallization mechanism
OH^-/SiO_2 ratio	silicate molecular weight
inorganic cations/SiO_2 ratio	structure; cation distribution
organic additives/SiO_2 ratio	structure; framework Al content

2.2.4.3 Templates

Cations (and hydrated cations) act as counter ions, but also have a templating effect. Templates stabilize the open framework by filling the empty space. The examples of added templates are amines and quaternary ammonium ions.

Goal: targeted synthesis of microporous structures by template control.



- Structure directing or templating agent
- Gel modifier (e.g. influencing Si/Al ratio)
- Void filler
- Change the formation and aging of gels
- Influence the crystallization process

Figure 2.6 Some representative ammonium or amino compounds used as organic additives in zeolite synthesis.

2.2.4.4 Templates as structure directing agents

Addition of other templates have increased the number of zeolite type structures prepared by leading to hitherto unknown zeolites and other microporous materials. Also, it has made it possible to synthesize zeolites with various Si/Al ratios, e.g. zeolite LTA with a Si/Al ratio > 1.

Clearly the template has a structure directing effect. But the templating effect is still not understood, and it is not possible to predict which zeolite structure is produced by a certain template.

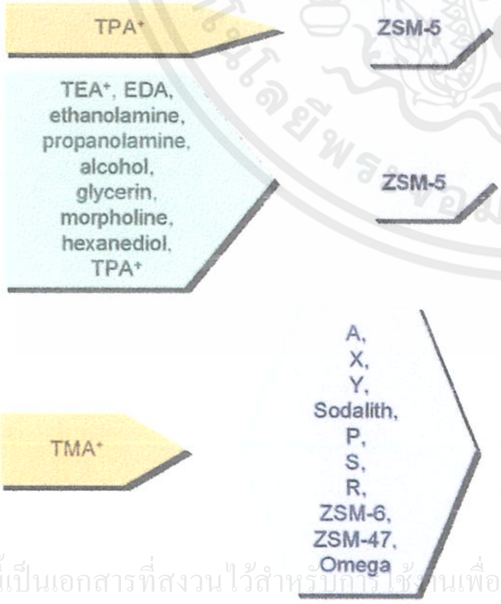


Figure 2.7 Template for zeolite

2.2.4.5 Zeolite (zeotype) structure

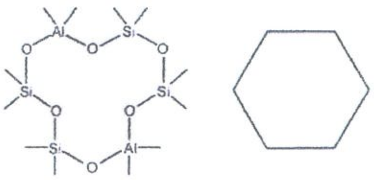


Figure 2.8 Six-membered ring structure of [SiO_4] and [Al_2O_3] tetrahedral (left) that can be found in zeolites, and its schematic representation as a CPU (right).

Representation of a six membered ring of TO4-tetrahedra (Contains 6 Si and 6 O)

- The basic (primary) building blocks are tetrahedra
- All tetrahedra share corners
- The arrangement of the building blocks is periodic (crystalline)

Building units:

- Primary or basic building units (BBU): Tetrahedron
- Secondary or composite building units (CBU): polymeric structures (rings, prisms etc.)
- Tertiary building units: Larger cages

The flexibility of the T-O-T bond angle (120-180°) allows a large number of CBUs to exist, and results in a wealth of different structures to be constructed.

2.2.4.6 CBUs

Zeolite structures may be seen as built from CBUs. For instance the ZSM-5 framework may be built from 5-1 units. It is important not to assume that the synthesis of zeotype materials occur via assembly of CBUs floating around in the synthesis mixture.

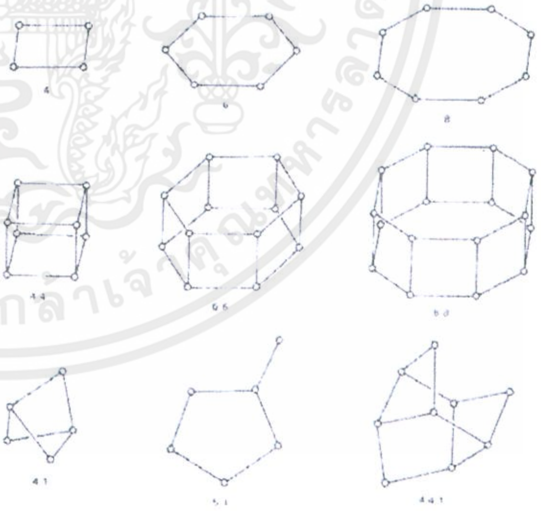


Figure 2.9 Composite building units (CBUs) found in zeolite structures.

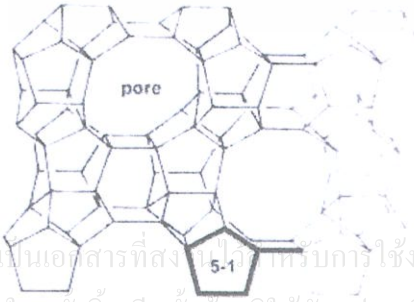
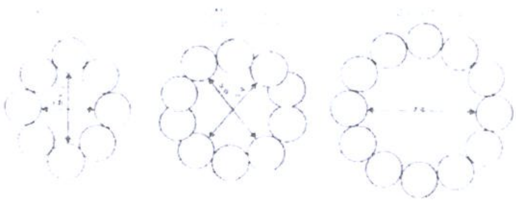


Figure 2.10 Network structure of ZSM-5.

2.2.4.7 Rings and pore size



Pore openings or rings in zeolites can be 8-, 10-, and 12-rings shown as connecting spheres. The openings may have various shapes, which influencing the kinetic diameter.

Figure 2.11 Examples of three of pore openings in zeolites: Erionite (left) contains an 8-ring pore opening, ZSM-5 (center) a 10-ring system, and type Y zeolite (right) a 12-ring pore system (the diameters are given in °A).

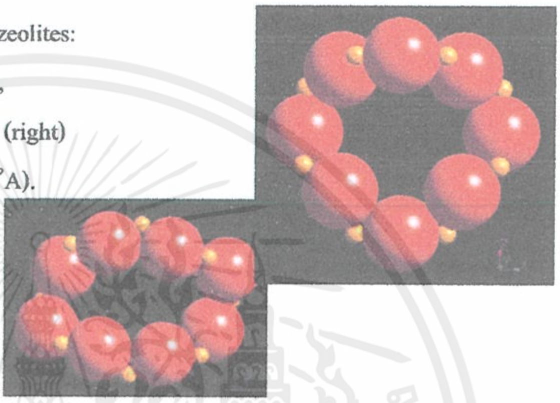


Figure 2.12 Analcime 8-ring (left) and edingtonite 8-ring (right)

2.2.4.8 Cages and channels

Zeolite LTA may be seen as built from the CBUs: 8, 4-4, 6-2, 6, 1-4-1, 4 . May be seen as built from interconnected sodalite cages (β-cages).

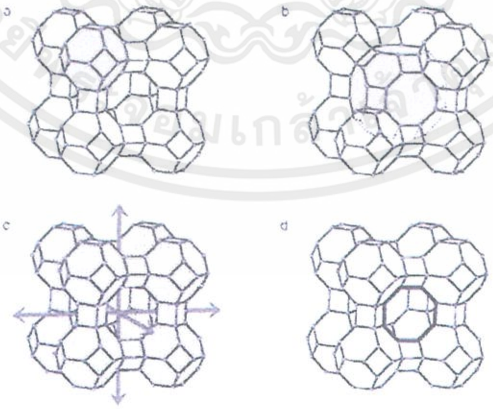


Figure 2.13 Features of the pores in zeolite A: a) the sodalite cage, b) the α-cavity, c) the three-dimensional channel system, and d) the 8-membered ring defining the effective channel width.

2.2.4.9 Linking CBUs, composite building units

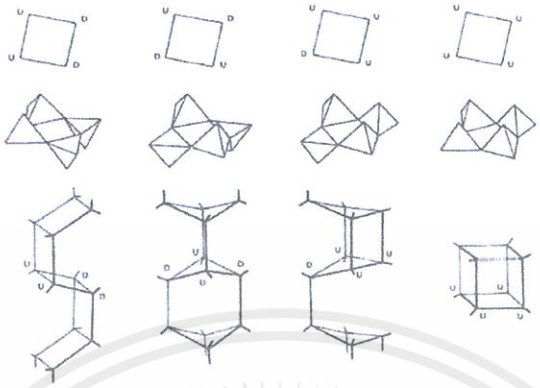


Figure 2.14 Possible linkages for the 4-membered ring CBU. Upper row: schematic representation of the CBU; U=up and D=down. Center row: the tetrahedral view. Bottom row: chain sequences formed from the differently oriented CBUs.

2.2.4.10 Dimensionality

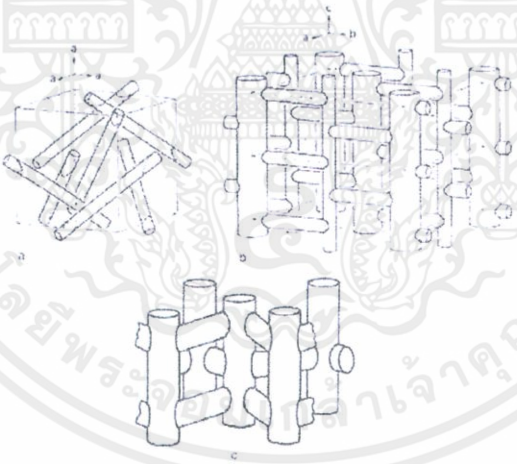


Figure 2.15 Channel representation for examples of one-, two-, and three-dimensional systems; a) analcime; b) mordenite; c) ZSM-5.

2.2.4.11 Zeolites: HZSM-5

ZSM-5 is an aluminosilicate zeolite belonging to the pentasil family of zeolites. Its chemical formula is $Na_nAl_nSi_{96-n}O_{192}\cdot16H_2O$ (0<n<27), patented by Mobil Oil Company in 1975. It is widely used in the petroleum industry as a heterogeneous catalyst for hydrocarbon isomerization reactions.

Structure

ZSM-5 is composed of several pentasil units linked together by oxygen bridges to form pentasil chains. A pentasil unit consists of eight five-membered rings. In these rings, the vertices are Al or Si and an O is assumed to be bonded between the vertices. The pentasil chains are interconnected by oxygen bridges to form corrugated sheets with 10-ring holes. Like the pentasil units, each 10-ring hole has Al or Si as vertices with an O assumed to be bonded between each vertex. Each corrugated sheet is connected by oxygen bridges to form a structure with "straight 10-ring channels running parallel to the corrugations and sinusoidal 10-ring channels perpendicular to the sheets." Adjacent layers of the sheets are related by an inversion point. The estimated pore size of the channel running parallel with the corrugations is 5.4–5.6 °A. The crystallographic unit cell of ZSM-5 has 96 T sites (Si or Al), 192 O sites, and a number of compensating cations depending on the Si/Al ratio, which ranges from 12 to infinity. The structure is orthorhombic (space group Pnma) at high temperatures, but a phase transition to the monoclinic space group $P2_1/n.1.13$ occurs on cooling below a transition temperature, located between 27 and 77 °C. ZSM-5 catalyst was first synthesized by Argauer and Landolt in 1972. It is a medium pore zeolite with channels defined by ten-membered rings. The synthesis involves three different solutions. The first solution is the source of alumina, sodium ions, and hydroxide ions; in the presence of excess base the alumina will form soluble $Al(OH)_4^-$ ions. The second solution has the tetrapropylammonium cation that acts as a templating agent. The third solution is the source of silica, one of the basic building blocks for the framework structure of a zeolite. Mixing the three solutions produces supersaturated tetrapropylammonium ZSM-5, which can be heated to recrystallize and produce a solid.

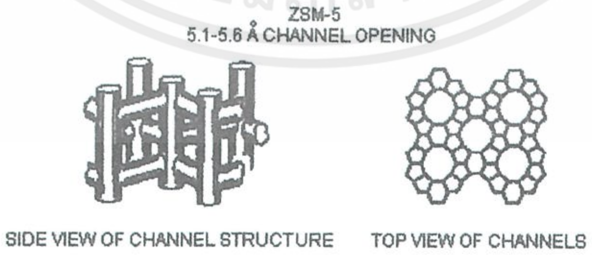


Figure 2.16 ZSM-5 structure

Synthesis

ZSM-5 is a synthetic zeolite, closely related to ZSM-11. There are many ways to synthesize ZSM-5, a common method is as follows:

$$SiO_2 + NaAlO_2 + NaOH + N(CH_2CH_2CH_3)_4Br + H_2O \longrightarrow \text{ZSM-5} + \text{analcime} + \text{alpha-quartz}$$

ZSM-5 is typically prepared at high temperature and high pressure in a Teflon-coated autoclave and can be prepared using varying ratios of SiO_2 and Al containing compounds.

Uses

ZSM-5 has a high silicon to aluminum ratio. Whenever an Al^{3+}cation replaces a Si^{4+}cation, an additional positive charge is required to keep the material charge-neutral. With proton (H^+) as the cation, the material becomes very acidic. Thus the acidity is proportional to the Al content. The very regular 3-D structure and the acidity of ZSM-5 can be utilized for acid-catalyzed reactions such as hydrocarbon isomerization and the alkylation of hydrocarbons. One such reaction is the isomerization of meta-xylene to para-xylene. Within the pores of the ZSM-5 zeolite, para-xylene has a much higher diffusion coefficient than meta-xylene. When the isomerization reaction is allowed to occur within the pores of ZSM-5, para-xylene is able to traverse along the pores of the zeolite, diffusing out of the catalyst very quickly. This size-selectivity allows the isomerization reaction to occur quickly in high yield.

Figure 2.17 Meta-xylene to para-xylene

ZSM-5 has been used as a support material for catalysis. In one such example, copper is deposited on the zeolite and a stream of ethanol is passed through at temperatures of 240 to 320 °C as a vapor stream, which causes the ethanol to oxidize to acetaldehyde; two hydrogens are lost by the ethanol as hydrogen gas. It appears that the specific pore size of ZSM-5 is of benefit to this process, which also functions for other alcohols and oxidations. The copper is occasionally combined with other metals, such as chromium, to fine tune the diversity and specificity of the products, as there is likely to be more than one. Acetic acid is an example of one possible byproduct from hot copper oxidation.

2.2.5 γ-Alumina as a Support for Catalysts

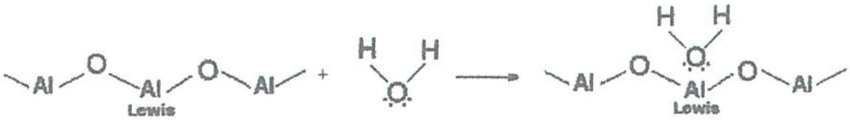
Among the different transition aluminas known, γ-alumina (γ-Al_2O_3) is perhaps the most important with direct application as a catalyst and catalyst support in the automotive and petroleum industries. The usefulness of this oxide can be traced to a favorable combination of its textural properties, such as surface area, pore volume, and pore size distribution and its acid/base characteristics, which are mainly related to surface chemical composition, local micro structure, and phase composition. Nevertheless, the chemical and hydrothermal stability of γ-Al_2O_3 are still a critical point for catalytic applications.

For example, the use of γ-Al_2O_3 as a support for Co based catalysts in the Fischer–Tropsch (FT) process for the production of clean fuels is not lacking in practical problems. The most common undesirable situations are: 1) alumina dissolution during supported catalyst preparation (usually in aqueous media), which affects the nature of the resulting Co species, 2) γ-Al_2O_3 rehydration during catalyst implementation because of the H_2O produced in the FT process, and 3) thermal degradation (sintering and phase transformation) in the catalyst regeneration step (hot spots). It is clear that these side-reactions, which affect catalyst stability, activity, and selectivity, are principally related to support stability.

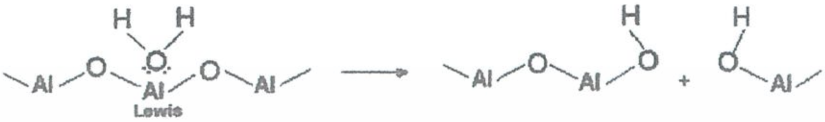
In the present work, the main aspects to be taken into account when trying to improve the properties of γ-Al_2O_3 as a support for catalysts are reviewed. First, the micro- and macroscopic nature of the support are described because without an adequate knowledge of them any applications will always be less than optimal. Next, the significance of the synthesis route is discussed, followed by the γ-Al_2O_3/H_2O interface and acid/base properties due to the effect of H_2O on support stability during both catalyst preparation and implementation. The importance of studying the oxide surface sorption behavior through the proton-affinity distributions is also considered. Finally, some practical implications for the Co/γ-Al_2O_3 system are presented.

γ-Al_2O_3/H_2O Interface

The existence of Lewis acid sites (cus cations) and basic sites (oxide anions) at the γ-Al_2O_3 surface allows its rehydroxylation (or rehydration) by interaction with H_2O, so that *cus* cations and anions can, in part, be converted into surface hydroxy groups. This interaction has been represented as a two-step process for γ-Al_2O_3 under atmospheric conditions that involves nondissociative adsorption of H_2O on Lewis sites (*cus* Al), which essentially consists in a transfer of electron density to a Lewis acid site.



Followed by dissociative chemisorption of H_2O and modification of surface Al coordination with the hydroxy group bonded to the Al atom, i.e., the two-coordinate oxygen atom adjacent to the Al site is protonated.



The rehydration of γ-alumina corresponds to the loss of tetrahedrally coordinated Al surface species and an increase of hydroxylated octahedral Al that can also involve some Al. The reactivity towards water depends on the layers exposed at each surface [10].

γ-Al_2O_3 as a Support

Transition aluminas are frequently used as pre-shaped supports for preparing multiphase catalysts that consist of an active phase dispersed on a carrier or support. The properties of the active phase depend mainly on the manner in which the active component of the catalyst (precursor) is introduced on to the support and the nature and strength of precursor–support interactions.

The major route for supported catalyst preparation makes use of aqueous media by simple impregnation (wet impregnation or incipient wetness) or by homogeneous deposition-precipitation, ion exchange, and specific adsorption. The choice of one or the other route is usually made by considering the nature and strength of the support-precursor interactions. Common subsequent steps are washing and drying, accompanied by irreversible transformation of the catalyst (its activation).

Different kinds of precursor–support interactions have been considered. Surface interactions for small ions are generally accepted to be predominantly electrostatic, which is supported by experimental results where the extent of adsorption of positive/negative ions increases with a pH rise/decrease. Nevertheless, some experimental evidence reflects exceptions from the simple rule of electrostatic adsorption with the existence of “specific” or “chemical” surface–adsorbate interactions that may compete with coulombic repulsion, as in the adsorption of cations such as Ni^{2+}, Co^{2+}, and Pb^{2+} onto a positively charged alumina surface. These results support the existence of specific sites on the hydroxylated surface that act in adsorption of the catalyst precursor and are related to the intrinsic acid/base properties of the surface. Moreover, the adsorption by ligand substitution, i.e., surface hydroxyls "become members" of the coordination sphere of the adsorbate, has been suggested for halide complexes of Pt, Pd, Rh, Ir, Au, and Ru on alumina and for amine complexes of Co^{2+}, Ni^{2+}, and Cu^{2+} on titania.

The surface density of adsorption sites is usually low, which gives a high metal dispersion but insufficient loading. Regulation of the adsorption capacity of amphoteric supports like γ-Al_2O_3 can be done by doping solid oxides with electropositive (Na^+, Li^+) or electronegative (F^-, Cl^-) ions, which results in an increase/decrease of the apparent *pzc* values of supports. However, the introduction of basic or acidic modifiers may also change important properties of the catalysts. Another possibility for increasing metal concentration is variation of the temperature of the impregnation solution.

In spite of the advantages of precursor impregnation from an aqueous phase, such as easy scale up at relatively low cost, the use of the metal is inefficient because of its incomplete loading and reduction and uncontrolled sintering during high-temperature salt decomposition. This has motivated researchers to study other ways to prepare supported catalysts, directed mainly at avoiding the use of H_2O as the impregnation phase. Organic media, vapor, and solid phases have been investigated. The most straight forward way for preparing dispersed metal catalysts consists in mounting metallic atoms or small clusters of metal atoms in their zero-valent state onto an appropriate support, which eliminates the need for any subsequent activation and the catalyst can be obtained in a single preparation step. For example, metallic Pt particles mounted on TiO_2 by means of a micro emulsion method have been reported recently. Metal–support interactions are not observed and the Pt/TiO_2 catalysts show higher catalytic activity than the same material prepared by the impregnation technique [11].

2.3 Propanol

1-Propanol is a primary alcohol with the formula $CH_3CH_2CH_2OH$. This colorless liquid is also known as propan-1-ol, 1-propyl alcohol, *n*-propyl alcohol, *n*-propanol, or simply propanol. It is an isomer of isopropanol (2-propanol, isopropyl alcohol). It is formed naturally in small amounts during many fermentation processes and used as a solvent in the pharmaceutical industry mainly for resins and cellulose esters.

Chemical properties

1-Propanol shows the normal reactions of a primary alcohol. Thus it can be converted to alkyl halides; for example red phosphorus and iodine produce *n*-propyl iodide in 80% yield, while PCl_3 with catalytic $ZnCl_2$ gives 1-chloropropane. Reaction with acetic acid in the presence of an H_2SO_4 catalyst under Fischer esterification conditions gives propyl acetate, while refluxing propanol overnight with formic acid alone can produce propyl formate in 65% yield. Oxidation of 1-propanol with $Na_2Cr_2O_7$ and H_2SO_4 gives only a 36% yield of propionaldehyde, and therefore for this type of reaction higher yielding methods using PCC or the Swern oxidation are recommended. Oxidation with chromic acid yields propionic acid.

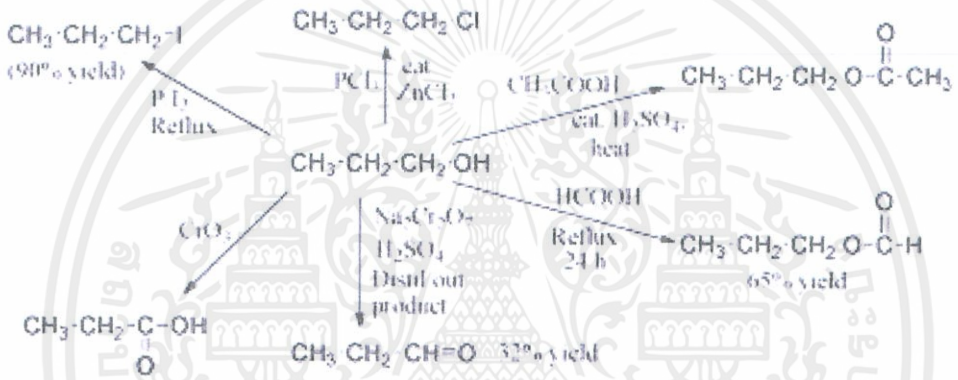


Figure 2.18 Normal reaction of n-propanol.

Preparation

1-Propanol is manufactured by catalytic hydrogenation of propionaldehyde. The propionaldehyde is itself produced via the oxo process, by hydroformylation of ethylene using carbon monoxide and hydrogen in the presence of a catalyst such as cobalt octacarbonyl or arhodium complex.

$H_2C{=}CH_2 + CO + H_2 \longrightarrow CH_3CH_2CH{=}O$

$CH_3CH_2CH{=}O + H_2 \longrightarrow CH_3CH_2CH_2OH$

A traditional laboratory preparation of 1-propanol involves treating *n*-propyl iodide with moist Ag_2O. 1-Propanol was discovered in 1853 by Chancel, who obtained it by fractional distillation of fuel oil. Indeed 1-propanol is a major constituent of fuel oil, a by-product formed from certain amino acids when potatoes or grains are fermented to produce ethanol. This process is no longer a significant source of 1-propanol [12].

2.4 Literature reviews

Nowadays, the study on conversion of low valued by-product to higher valued chemicals is interesting. One of the main focuses is the by-products from biomass conversion particularly, acetol (hydroxyacetone) that is by-product from glycerol conversion [13]. Acetol can be converted to n-propanol by hydrodeoxygenation via hydrogenation to 1,2-propanediol followed by dehydration to propanaldehyde and then hydrogenation to n-propanol [14]. As shown in **Figure 2.19**.

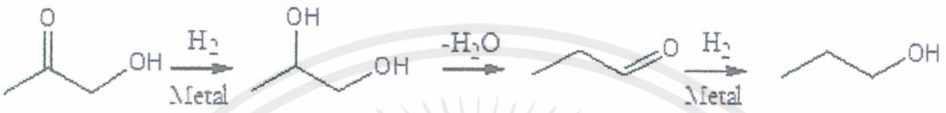


Figure 2.19 Pathways of acetol to n-propanol

In the previous work, hydrodeoxygenation of glycerol produce 1,2-propanediol as major product. Acetol (hydroxyacetone) has found to be an intermediate in the conversion of glycerol into 1,2-propanediol through the dehydration–hydrogenation reactions. One effective operation is a two-step process composing dehydration of glycerol over acidic support and subsequence hydrogenation over metal catalysts such as Cu and Ni under hydrogen pressure [14,15]. 1,2-propanediol is more preferable as a substrate for the production of n-propanol. The catalysts for the selective hydrogenolysis of glycerol to 1,3-propanediol have a potential in the production of n-propanol from glycerol. However, these systems need high pressure of hydrogen and Rh or Pt based catalysts, which are expensive. Zhang et al. [6] found that zeolites and metal can catalyze 1,2-propanediol into n-propanol at 250–300 $^{\circ}C$ at ambient pressure under hydrogen [16]. The catalytic dehydration of methanol to DME has been studied over ZSM-5 and mordenite catalysts with different pore structures and acidities. The promotional aspects of the Na modified catalyst are attributed to the significant reduction in surface density and nature of the strong acid-sites with increase in Na loading in MDHC-1, making the catalyst more resistant towards hydrocarbon formation [17]. Moreover, other porous material such as alumina can be dehydration. In the previous work, alumina has been study on dehydration of ethanol [18] and methanol [19]. And the result show that gamma alumina can dehydration because it has Lewis acid site in their structure.

Accordingly, hydrogenation of acetol can be done over promoted metals such as Cu, Ni, Pt and Pd and dehydration function can be achieved over acidic catalyst. Hence, bi-functional catalyst is suitable for this reaction.

CHAPTER 3

EXPERIMENTAL

3.1 Chemical reagents

Chemical reagents	Grade of purity	Manufacturers
1. Nickel (II) nitrate hexahydrate	99%	Carlo ERBA
2. Copper (II) nitrate trihydrate	99.5%	QRPC
3. NH_4-ZSM-5 (Si/Al = 28)		Zeolyst international
4. Aluminium hydroxide	62-67%	Unilab
5. Hydroxy acetone	90%	Aldrich
6. Distillation water		

3.2 Apparatus and instruments

1. Catalytic testing rig
2. Gas adsorption analyzer (Autosorb-1C, Quantrachrome)
3. Gas chromatograph (VARIAN CP-3800)
4. Laboratory glassware
5. Laboratory plasticware
6. Mass flow controller model
7. Oven
8. Sieve
9. Syringe pump
10. Temperature programmed reduction (TPR) system model
11. Temperature programmed desorption (TPD) system model
12. Tube furnace with a programmable temperature controller
13. X-ray fluorescence spectrometer (Siemens: SRS3400, Scientific Instrument Service Centre, KMIT'L)

3.3 Process of study

A process of the study on the preparation of the catalysts with metal loading on support and catalyst comprises the following stages:

3.3.1 Synthesis and modification of catalysts

Modification of copper and nickel support H-ZSM-5 and gamma-alumina (Ni-Cu/H-ZSM-5 and Ni-Cu/γ-Al_2O_3) with 35%wt. metal loading by wet impregnation method.

3.3.2 Characterization of catalysts

3.3.2.1 Determine chemical composition of the catalysts by X-ray fluorescence (XRF)

3.3.2.2 Determine the surface area and pore size by gas adsorption analysis (Autosorp).

3.3.2.3 Investigate reducibility of the active sites by H_2-Temperature programmed reduction (TPR).

3.3.2.4 Determine the acidity of the catalysts by NH_3-Temperature programmed desorption (NH_3-TPD).

3.3.3 Catalytic testing

3.3.3.1 Investigate the product distribution.

3.3.3.2 Investigate the effect of catalysts mixing with support.

3.3.3.3 Investigate the effect of reaction temperature.

3.3.3.4 Investigate the contact time of reaction.

3.3.3.5 Investigate the deactivation of the catalysts.

3.3.4 Products analysis

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

3.4 Synthesis and modification

Synthesis of 35%wt. Nickel-Copper supported H-ZSM-5 catalysts (Ni-Cu/H-ZSM-5) and 35%wt. Nickel-Copper supported alumina catalysts (Ni-Cu/Al_2O_3) by wet impregnation method.

Supported Ni/Cu catalysts were prepared by followings: support calcination, precursor solution preparation, support impregnation and supported precursor calcination. Catalyst of 35%wt. Ni-Cu/H-ZSM-5 (10.0 g), which has 20%wt. Ni and 15%wt. Cu, was prepared using the following steps and concentrations.

9.9 g of $Ni(NO_3)_2{:}6H_2O$ and 5.7 g of $Cu(NO_3)_2{:}3H_2O$ were dissolved in 58 ml of water to make metal solution at 1 M. A powder of NH_4-ZSM-5 was calcined in tube furnace with a programmable temperature controller at 450 °C for 5 h to make proton form that is H-ZSM-5. After that, 6.5 g of H-ZSM-5 was impregnated with the Ni-Cu precursor solution in plastic beaker. The mixture was gradually dried in water bath with heated by hotplate at 100 °C to remove excess water till support almost dry and the catalyst was calcined in tube furnace at 450 °C for 5 h. The Ni and Cu loadings were confirmed by XRF analysis.

Catalyst of 35%wt. Ni-Cu/Al_2O_3 (10.0 g) were prepared using the same procedure as described above except a powder of aluminium hydroxide was calcined in tube furnace at 550 °C for 5 h to make γ-Al_2O_3.

3.5 Characterization of catalysts

3.5.1 X-ray fluorescence

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. Each element has electronic orbitals of characteristic energy. The removal of an inner electron by an energetic photon is provided by a primary radiation source, following by the moving of an electron from an outer shell into that vacancy and released energy call secondary electron or fluorescent. The released energy is a characteristic radiation that tells the composition of the sample. This technique can be done according to the following procedure: the catalyst sample was weighed about 0.5 g and boric acid was weighted about 4.5 g, then sample and boric acid were mixed together, and compressed into alumina pan before bring into the XRF sample holder in XRF instrument.

3.5.2 Gas adsorption analysis

Gas adsorption analysis is the technique generally used for determining surface area and pore size distribution of solid catalyst. This technique can be done according to the following procedure: the catalyst sample was weighed about 100 mg and transferred to a cleaned, dried sample cell. This sample cell was attached to the outgassing station. Then, a heating mantle was installed with the sample cell and the temperature was raised to 300 °C for 12 hours. After the residual gas was removed by heating under vacuum, nitrogen adsorbate was filled by opening the gas inlet valve. The sample cell was attached to the sample station. Initially, a dewar flask of liquid nitrogen was placed around the sample cell. Nitrogen adsorbate pressure can be regulated by 1 torr transducer with 3 minutes equilibration time and 0 scaled tolerances. When the adsorption was completed, the sample cell was removed from the sample station, dried thoroughly and reweighed.

3.5.3 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 0.1 g 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 for 3 hours (25 ml/min) and cooled to 50 °C. The heating rate of 2°C/min, the H_2 in Ar flow of 25 ml/min is applied for TPR analysis. Water produced during the reduction process was removed in a U-shape glass trap at -70 °C (vapor of liquid N_2) before entering the TCD.

3.5.4 Temperature programmed desorption

Ammonia is probably the most frequently used probe molecule for acidity assessment. Its small molecular size allows one to probe almost all acid sites of both micro and mesoporous materials. NH_3-temperature-programmed desorption (NH_3-TPD) experiments were carried out using a TCD detector. Before adsorption, the sample (0.2 g) were heated to its calcinations temperature in air zero for 2 hours (30 ml/min) and cooled to 30 °C. Adsorption of NH_3 was performed at 30 °C. After saturation, the sample were flushed with He at this temperature for 1 hours. TPD measurements were done from 35 to 800 °C with a heating rate of 10 °C/min, using He as a carrier gas.

3.6 Catalytic testing

Gas phase catalytic conversion of acetol can be investigated at atmospheric pressure in a continuous fixed-bed down flow reactor made with glass tube (8 mm O.D.). The catalyst bed was packed by glass wool in the middle of the reactor. The reactor was installed onto the catalytic test rig which was located inside a temperature-controlled furnace. The gas flows was controlled by mass flow controllers and checked by bubble flow meter. Before activity testing, the catalyst was activated by heating at 2°C/min to its calcinations temperature (450 °C) and hold at that temperature for 2 hours under the steam of air zero (30 ml/min). The reactor was cooled to the reduction temperature (400 °C) and hold at this temperature for 4 hours under H_2 flow (30 ml/min). The reactor was cooled to the reaction temperature (200 °C) under a flow of N_2 and then purged with carrier gas (30 ml/min of H_2) for 10 minutes prior to the reaction.

In each run, acetol was passed through the catalyst bed by a 30 ml/min flow of H_2. The catalytic test was continued for at least 6 hours on stream. The product effluents were trapped at 5-10 °C using ice. Description of the reaction set up and the reaction condition are summarized in **Table 3.1**. The schematic diagram of the experimental setup is shown in **Figure 3.1**.

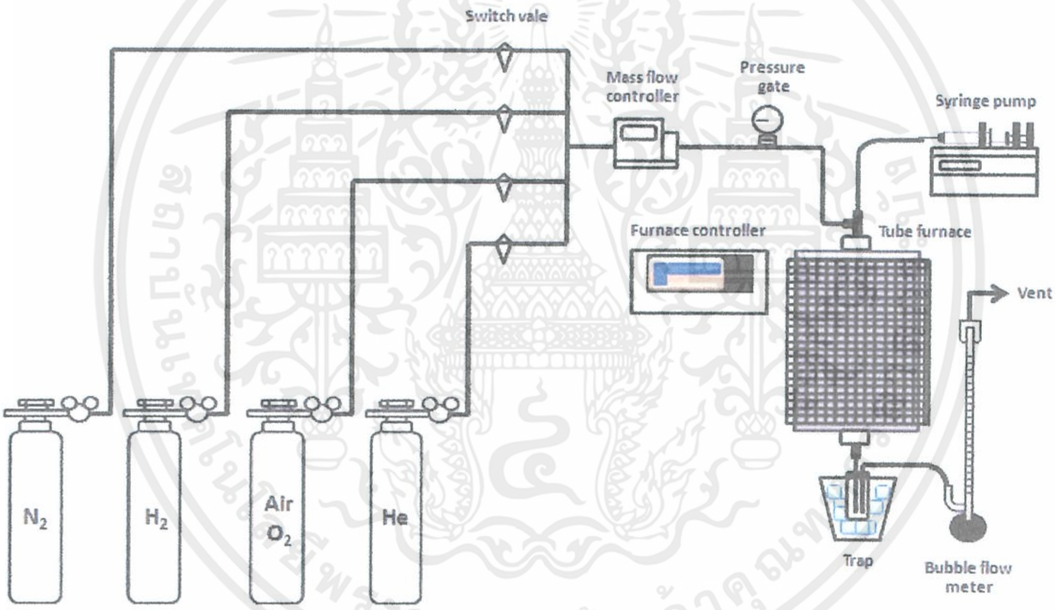


Figure 3.1 The schematic diagram of the catalytic testing rig.

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

Parameters	Value
Reactor inside diameter (mm)	6
Reactor outside diameter (mm)	8
Total flow (ml/min)	~30
Bed length (cm)	30
Catalyst weight (g)	0.08
Contact time: W/F (g.h/mol)	13, 40, 67 and 94
Catalyst size (μm)	600-850
Catalyst activation (before reaction)	Heating rate: 2 °C/min Heat treatment: 450 °C hold for 2 hours Gas: air zero (30 ml/min)
Carrier gas	H_2
Reaction temperature	200-300 °C
Total reaction pressure	Atmospheric pressure

3.7 Product testing

The product of hydrodeoxygenation acetol to n-propanol was trapped from reactor by ice and analyzed with a gas chromatograph (VARIAN CP-3800) with flame ionization detector (GC-FID) and a capillary column DB-WAX (length, 30 m ; internal diameter, 0.25 mm ; film thickness, 0.25 um). The following temperature program was used for the analysis of liquid hydrocarbon: linear velocity is 21.9 cm/sec, 60 °C hold for 2 min, then ramp at 8 °C/min to 200 °C and hold at this temperature for 0.5 min by use N_2 as carrier gas.

CHAPTER 4

RESULTS AND DISCUSSION

Catalyst characterization

Elemental composition of the catalysts were determined by X-ray fluorescence spectroscopy and surface area were determined by N_2-physisorption as shown in **Table 4.1**

Table 4.1 Elemental analysis and N_2-physisorption data of 35%wt. Ni-Cu/H-ZSM-5 and 35%wt. Ni-Cu/Al_2O_3 catalysts

Catalysts	35%wt. Ni-Cu/H-ZSM-5	35%wt. Ni-Cu/Al_2O_3
Ni (wt.%)	23.2	28.9
Cu (wt.%)	19.0	23.6
Ni+Cu (wt.%)	42.2	52.5
Al (wt.%)	0.7	17.8
Si (wt.%)	21.1	-
Ni/Cu ratio	1.2	1.2
Si/Al ratio	27.6	-
S_{BET} (m^2/g)	240	109
Micropores size (nm)	< 1.4	-
Mesopores size (nm)	3.8	4.3, 30.7

These values are calculated from elemental analysis as shown in **Appendix A**. It can be seen that Ni and Cu loading in the catalysts are higher than the expected value; that is 20%wt. and 15%wt., respectively. This means that the metal content in the catalysts was not precisely controlled by wet impregnation method. Nevertheless, it is interesting to observe that Ni/Cu ratio values of both catalysts were similar. It is also found that Si/Al ratio of 35%wt. Ni-Cu/H-ZSM-5, which is 27.6 is similar to that of the parent H-ZSM-5.

The N_2-physisorption isotherm of both catalysts presented micropores and mesopores as shown in **Figure 4.1**.

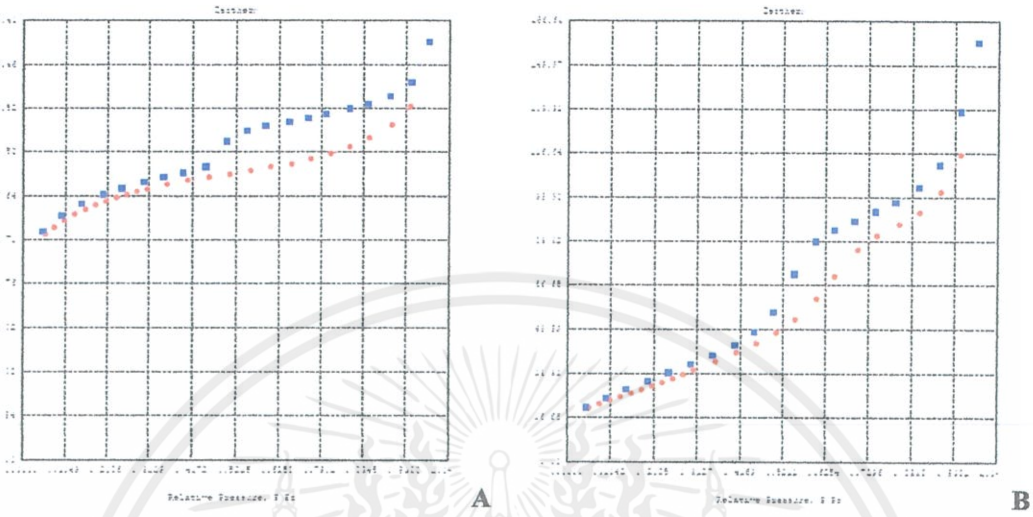


Figure 4.1 Isotherm of N_2-physisorption over 35%wt. Ni-Cu/H-ZSM-5 catalyst (A) and 35%wt. Ni-Cu/Al_2O_3 catalyst (B)

In fact, N_2 adsorption of H-ZSM-5 is mainly contributed from micropores. However, mesopores of H-ZSM-5 is the result of inter-particle voids of agglomerated crystallites. In contrast, the isotherm of 35%wt. Ni-Cu/Al_2O_3 catalyst exhibits mainly mesopores from both intra- and inter-particle voids. Pore size distributions were shown in **Appendix B**.

The TPR analysis of calcined 35%wt. Ni-Cu/H-ZSM-5 and 35%wt. Ni-Cu/Al_2O_3 catalysts presented major peaks at 180-380 °C as shown in **Figure 4.2.**

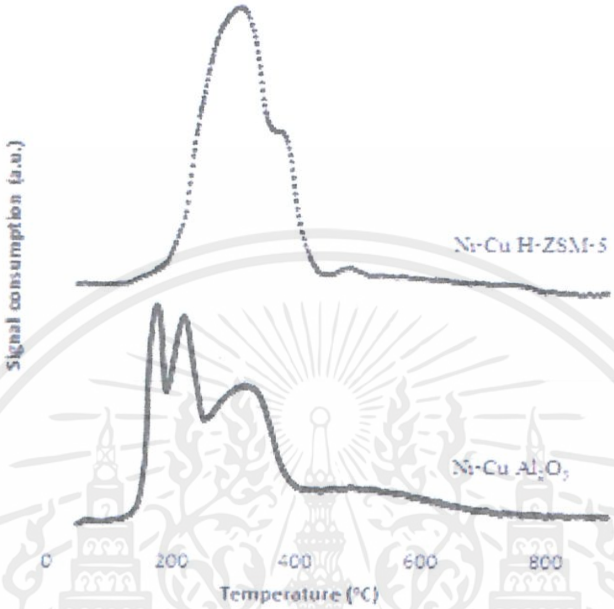


Figure 4.2 TPR profiles of calcined 35%wt. Ni-Cu/H-ZSM-5 and 35%wt. Ni-Cu/Al_2O_3 catalysts

The different temperature in TPR profile of both catalysts is resulted from the different interaction between metals oxide aggregates on the support. For 35%wt. Ni-Cu/H-ZSM-5 catalyst, the peak at 300 °C was attributed to the reduction of nickel-copper alloy as observed previously [7], suggesting that Ni has strong interaction with Cu. However, the excess Ni metal is separately dispersed on the H-ZSM-5 as show in reduction peak at 380 °C. For 35%wt. Ni-Cu/Al_2O_3 catalyst, three reduction peaks at 180°C and 220 °C are attributed to the reduction of Cu^{2+} to Cu^{1+} species and Cu^{1+} species to Cu^0 metal, respectively. While, the peak at 350 °C can be referred to nickel-copper alloy. The board peak in the temperature range of 400-700 °C exhibits reduction of Al_2NiO_4 species. It is suggested that Ni have a good interaction with Al_2O_3. Hence, relatively lower Ni-Cu alloy is found over this catalyst. Moreover, the excess Cu metal separately occluded on the Al_2O_3 support.

The NH_3-TPD of 35%wt. Ni-Cu/H-ZSM-5 and 35%wt. Ni-Cu/Al_2O_3 catalysts are shown in **Figure 4.3**.

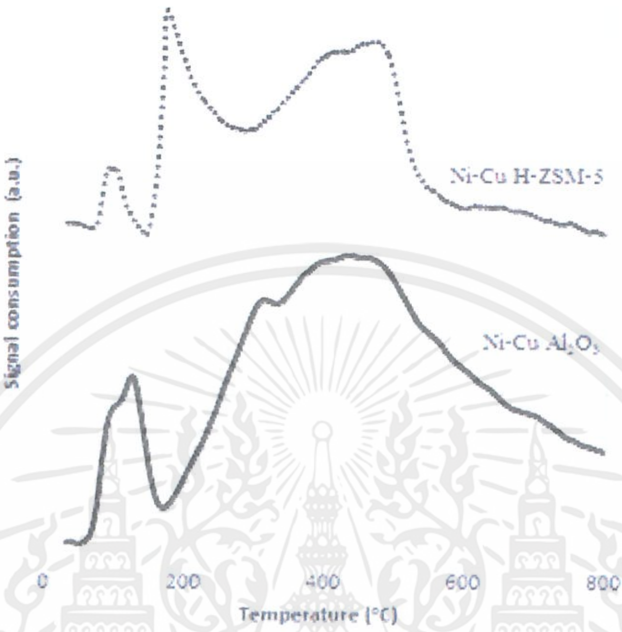


Figure 4.3 NH_3-TPD profiles of reduced 35%wt. Ni-Cu/H-ZSM-5 and 35%wt. Ni-Cu/Al_2O_3 catalysts

It was observed that the desorption of ammonia physisorbed on the surfaces take place at 100 °C for both catalysts. The peak at 200 °C can be referred to acid sites and the peak around 300-800 °C was an ammonia desorption from the defect framework of alumina in the structure [20], [21]. It is clear that the acidity of Ni-Cu/H-ZSM-5 catalyst as seen from the peak at 200 °C is higher than that of Ni-Cu/Al_2O_3 catalyst. This is presumably due to the bridging hydroxyl (Bronsted acid) of the zeolite.

Table 4.2 TGA of spent 35%wt. Ni-Cu/H-ZSM-5 catalyst at different contact times and temperatures.

Contact time (g.h/mol)	Reaction temperature ($^{\circ}$C)	Temperature ($^{\circ}$C)	Weight loss (%)
19	200	130-380	4.71
94	200	130-380	4.81
47	175	130-380	4.86
47	225	130-380	4.93

It was observed that at the same reaction temperature, the catalyst that runs at high contact time shows weight loss higher than that of at low contact time. This is because high conversion gives higher concentration of product retained on the catalyst surface. Moreover, at the same contact time, the catalyst that runs at high temperature shows weight loss higher than that of at low temperature, due to the high conversion as discussed previously.

Hydrodeoxygenation of acetol over supported Ni/Cu catalysts

Product distribution at various contact times from the hydrodeoxygenation of acetol over 35%wt. Ni-Cu/H-ZSM-5 catalyst was shown in **Figure 4.4**

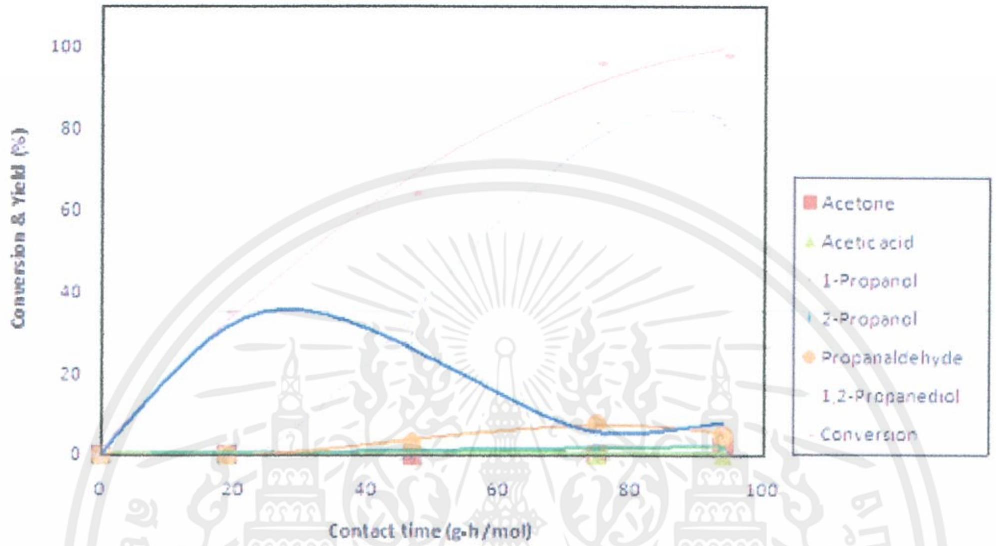


Figure 4.4 Conversion of acetol and yield of products from the reaction over 35%wt. Ni-Cu/H-ZSM-5 catalyst at the first hour of reaction as a function of contact time.

Reaction condition; Catalyst: 35%wt. Ni-Cu/H-ZSM-5, Temperature: 200 °C,

Contact time: 19-94 g.h/mol, Ambient pressure, 30 ml/min of hydrogen

It is clear that the conversion of acetol (hydroxyacetone) was 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. At low contact time, acetol can only be hydrogenated to 1,2-propanediol suggesting a strong interaction of the acetol with the metal surface. As the contact time was increased, 1,2-propanediol was decreased while 1-propanol was increasingly observed. It is clear that 1,2-propanediol can readily dehydrated to propanaldehyde over the proximated acid site and the dehydrated product (propanaldehyde) is promptly hydrogenated by the hydrogen spilled over to form 1-propanol as observed. Accordingly propanaldehyde was not found at low contact time. However, propanaldehyde appeared at high contact time because there is higher concentration of propanaldehyde on the surface. As hydrogen spilled over is limited, some of propanaldehyde can be retained and desorbed.

Acetone and 2-propanol were also detected at high contact time. This is because 1,2-propanediol can be dehydrated to acetone via protonation at the primary hydroxyl group. Accordingly the acetone formed by such pathway can undergo hydrogenation to 2-propanol in a manner similar to those discussed for 1-propanol. Small amount of acetic acid (<1%) was also found in the reaction. This can be attributed to the catalytic C–C bond cleavage of acetol over acid sites [2, 13]. From the study on the effect of contact time, the overall reaction pathways for acetol conversion over 35%wt. Ni-Cu/H-ZSM-5 catalyst can be proposed as shown in **Figure 4.5**.

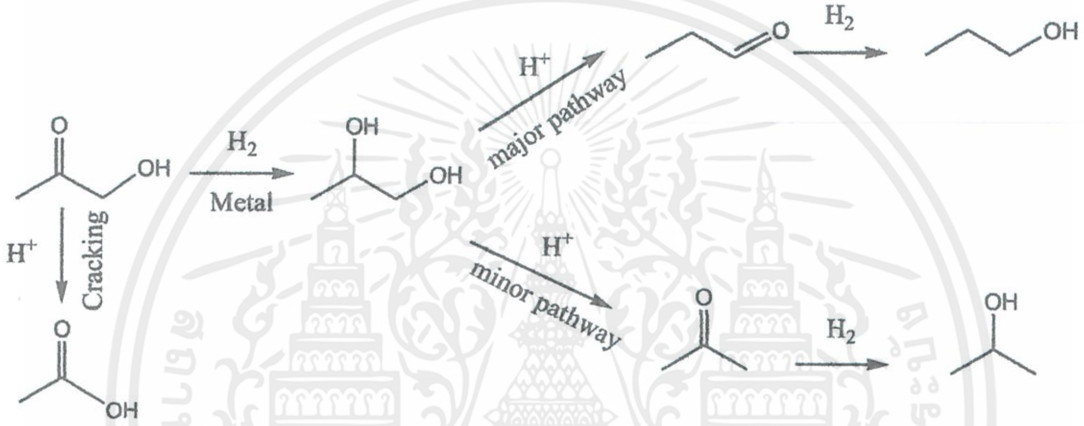


Figure 4.5 Reaction pathways

It is worth noting that, at low contact time, the conversion of acetol was relatively steady and only 1,2-propanediol was found as product as shown in **Figure 4.6 (A)**.

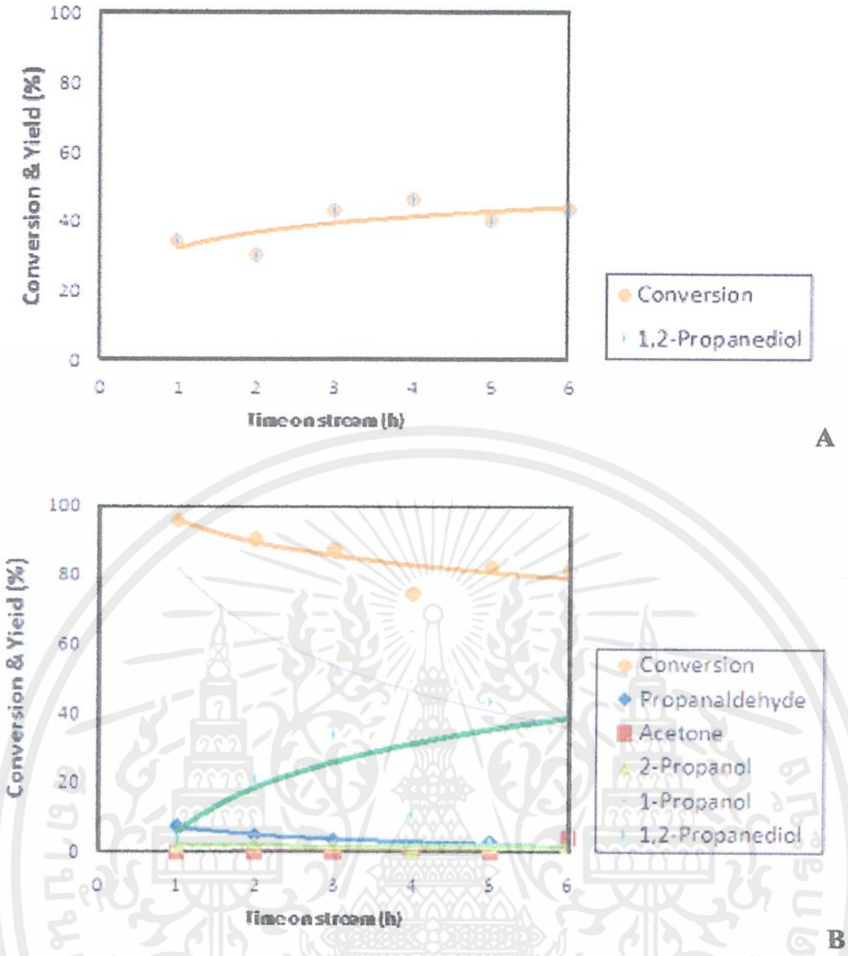


Figure 4.6 The acetol conversion over 35%wt. Ni-Cu/H-ZSM-5 catalyst as a function of time on stream at contact time = 19 g.h/mol (A) and contact time = 75 g.h/mol (B)

Reaction condition; Catalyst: 35%wt. Ni-Cu/H-ZSM-5, Temperature: 200 °C, Ambient pressure, 30 ml/min of hydrogen

However, at high contact time, the conversion of acetol was decreased with time on stream as shown in **Figure 4.6 (B)**. Yield of 1-propanol was decreased while the yield of 1,2-propanediol was increased. It is suggested that propanaldehyde, formed by dehydration of 1,2-propanediol, strongly interacted with the acid sites of the catalyst. As the reaction proceeds, the retained propanaldehyde can convert to higher molecular weight compounds by aldol condensation. Such higher molecular weight species or coke can be strongly adsorbed on acid sites diminishing dehydration activity. Therefore, 1,2-propanediol cannot be dehydrated to propanaldehyde as the acid sites is deactivated, leading to the significant decrease in 1-propanol yield over time on stream. Moreover the coke that form over the acid sites can affect to the metal surfaces leading to a reduce hydrogenation activity. Hence, the conversion of acetol was slightly decreased.

With the same reaction condition, 35%wt. Ni-Cu/H-ZSM-5 catalyst (A) and 35%wt. Ni-Cu/Al_2O_3 catalyst (B) were compared as shown in **Figure 4.7.**

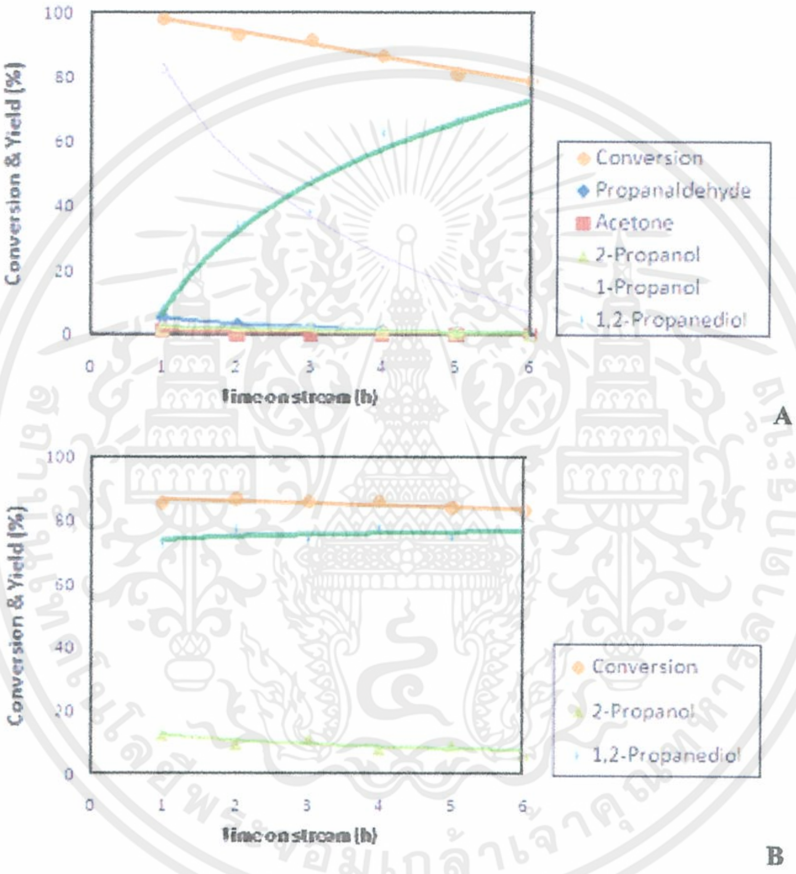


Figure 4.7 The acetol conversion over 35%wt. Ni-Cu/H-ZSM-5 catalyst (A) and 35%wt. Ni-Cu/Al_2O_3 catalyst (B) as a function of time on stream at contact time = 94 g.h/mol. *Reaction conditions; Catalyst: 35%wt. Ni-Cu/Al_2O_3 0.14 g, Temperature: 200 °C, Feed: 1.575 g/h of acetol at 7 %wt., Ambient pressure, 30 ml/min of hydrogen.*

It can be seen that 35%wt. Ni-Cu/H-ZSM-5 catalyst had greater activity to acetol hydrogenation as paralleled with 35%wt. Ni-Cu/Al_2O_3 catalyst. This is because there is more available Ni-Cu metallic surface on 35%wt. Ni-Cu/H-ZSM-5 catalyst as compared to that in

35%wt. Ni-Cu/Al_2O_3 catalyst (as discussed in TPR experiment). However, the conversion of acetol over 35%wt. Ni-Cu/H-ZSM-5 catalyst was decreased with time on stream as discussed earlier while the conversion of acetol over 35%wt. Ni-Cu/Al_2O_3 catalyst was relatively steady. This is because the 35%wt. Ni-Cu/Al_2O_3 catalyst possesses a low acidity (as shown in NH_3-TPD experiment) and low dehydration activity. Hence, the aldol condensation of the dehydrated product to form higher molecular weight compound or coke cannot be promoted. In addition, the products from dehydration over 35%wt. Ni-Cu/Al_2O_3 catalysts were different from those in 35%wt. Ni-Cu/H-ZSM-5 catalyst.

Instead of 1-propanol, 2-propanol was produced presumably because 35%wt. Ni-Cu/Al_2O_3 catalyst possesses Lewis acid sites that can convert 1,2-propanediol to 2-propanol by protonation at primary hydroxyl group. These is confirmed by feeding 1,2-propanediol over the two catalysts as shown in **Figure 4.8.**

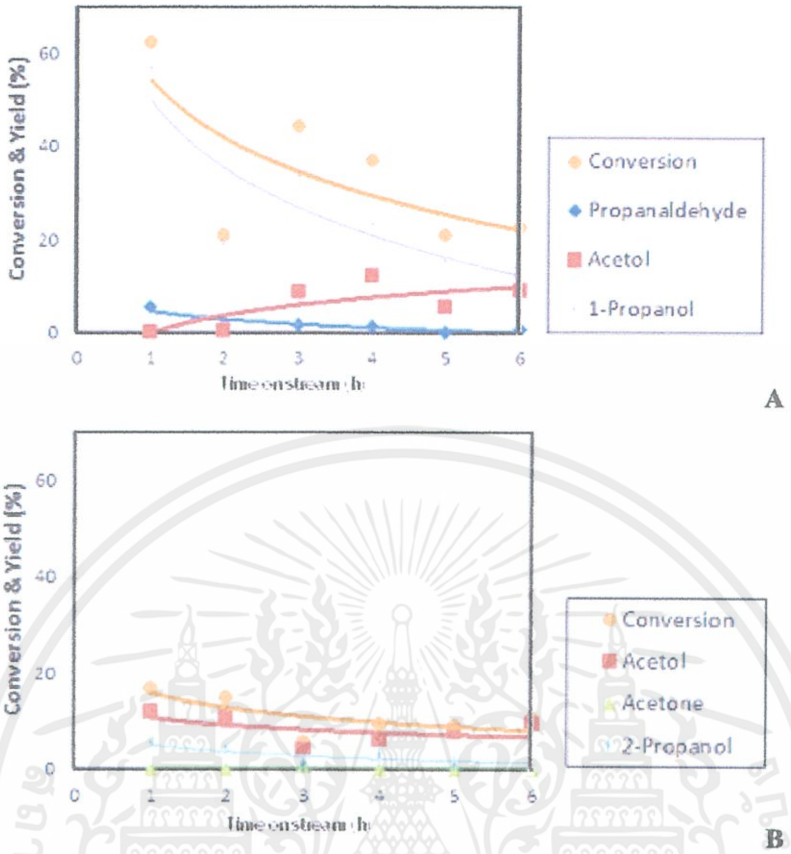


Figure 4.8 The 1,2-propanediol conversion over 35%wt. Ni-Cu/H-ZSM-5 catalyst (A) and 35%wt. Ni-Cu/Al_2O_3 catalyst (B) as a function of time on stream at contact time = 47 g.h/mol. *Reaction conditions ; Catalyst: 0.10 g, Temperature: 200 °C, Feed: 1.575 g/h of 1,2-propanediol at 10.25 %wt., Ambient pressure, 30 ml/min of hydrogen.*

It can be seen that the conversion of 1,2-propanediol over 35%wt. Ni-Cu/H-ZSM-5 catalyst (A) produced 1-propanol while 35%wt. Ni-Cu/Al_2O_3 catalyst (B) produced 2-propanol. Therefore the dehydration function of the two catalysts was different. This is because Ni-Cu/ H-ZSM-5 catalyst possesses Bronsted acid sites that tend to protonate the secondary hydroxyl group while the Lewis acid sites of Ni-Cu/Al_2O_3 catalyst tend to protonate at primary hydroxyl group. As the Ni-Cu/H-ZSM-5 catalyst possesses acidity higher than that of Ni-Cu/Al_2O_3 catalyst, the conversion of 1,2-propanediol over 35% wt. Ni-Cu/H-ZSM-5 catalysts (A) was higher than that of 35%wt. Ni-Cu/Al_2O_3 catalyst (B). However, 35%wt. Ni-Cu/H-ZSM-5 catalyst was rapidly deactivated due to the formation of high molecular weight product as discussed earlier.

It was noticed that acetol appeared as product for both catalysts. This is because, acetol can be produced from dehydrogenation of 1,2-propanediol over the metal surfaces as shown in **Figure 4.9**.

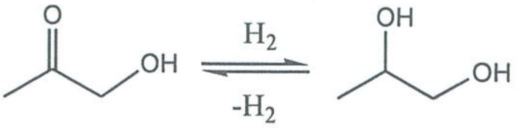


Figure 4.9 Acetol to 1,2-propanediol

It was also observed that acetol was increased when the Ni-Cu/H-ZSM-5 catalyst was deactivated. At the beginning 1,2-propanediol strongly adsorbed on the acid sites of catalyst and can be dehydrated to propanaldehyde followed by hydrogenation to 1-propanol. However, when the catalyst was deactivated, dehydration activity is reduced by the formation of higher molecular weight compound. Hence 1,2-propanediol cannot be adsorbed on acid sites, but may adsorb on metal sites leading to dehydrogenation to acetol. In contrast the 1,2-propanediol can be readily adsorbed on metal sites of Ni-Cu/Al_2O_3 catalyst and dehydrogenated to acetol. This is clear that the nature of acid sites distinctively effected to dehydration activity and hence product selectivity.

As hydrogenation is thermodynamically favored at low temperature and the dehydration is favored at high temperature. Accordingly, hydrodeoxygenation of acetol to 1-propanol may largely be effected by reaction temperature as seen in **Figure 4.10.**

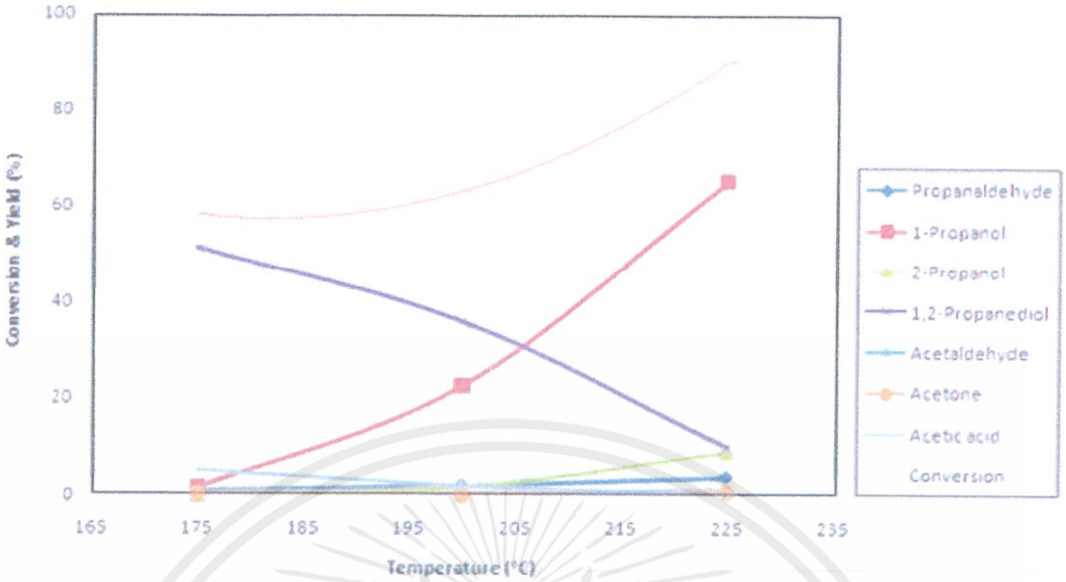


Figure 4.10 The effect of reaction temperature with conversion of acetol over 35%wt. Ni-Cu/H-ZSM-5 catalyst at average three first hours of reaction. *Reaction condition; Catalyst: 35%wt. Ni-Cu/H-ZSM-5 0.10 g, Temperature: 175-200 °C, Contact time: 47 g.h/mol, Feed: 1.575 g/h of acetol at 10 %wt., Ambient pressure, 30 ml/min of hydrogen.*

The result shows that the conversion of acetol increased with an increase in the reaction temperature. At low temperature, 1,2-propanediol was a main product and propanaldehyde was not produced. This is because the dehydration required high activation energy. As temperature was increased, dehydration of 1,2-propanediol to propanaldehyde and/or acetone can be promoted leading to a decreased in 1,2-propanediol yield. At the same time, the hydrogenation of the dehydrated products (propanaldehyde and/or acetone) can be facilitated at higher temperature leading to increased yield of 1-propanol and/or 2-propanol as observed.

However it was observed that higher deactivation can be observed for reaction at high temperature as shown in **Figure 4.11.** This is because propanaldehyde was promoted at high temperature leading to deactivation, as mentioned earlier.

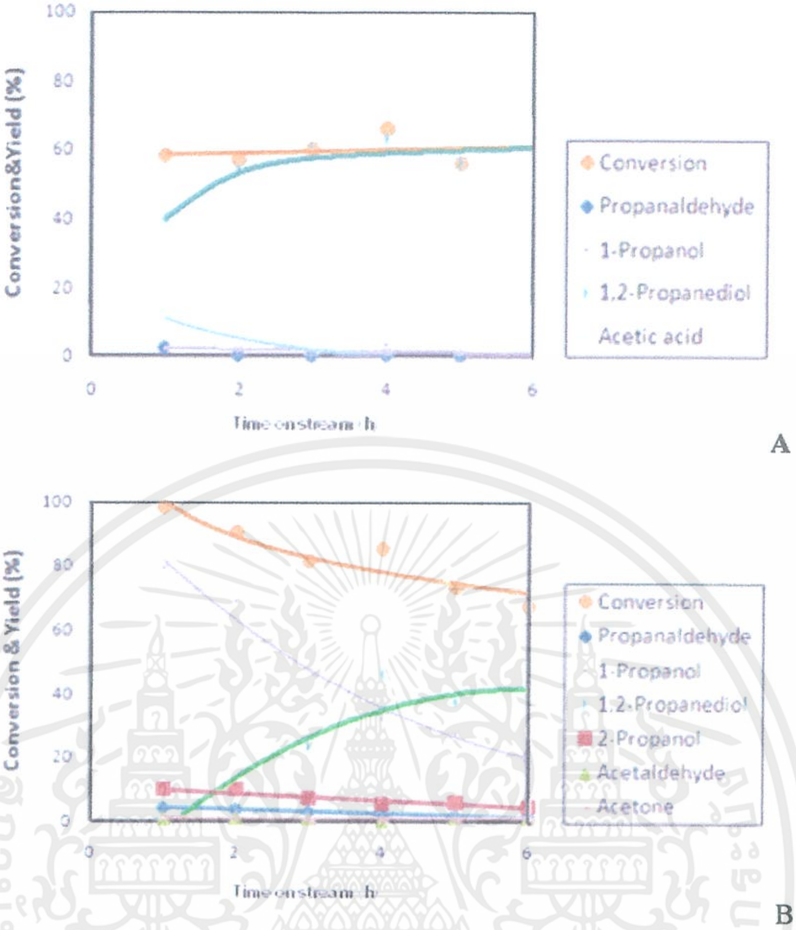


Figure 4.11 The acetol conversion over 35%wt. Ni-Cu/H-ZSM-5 catalyst as a function of time on stream at 175 °C (A) and 225 °C (B).

Reaction conditions ; Catalyst: 35%wt. Ni-Cu/H-ZSM-5 0.10 g, Contact time: 47 g.h/mol, Feed: 1.575 g/h of acetol at 10 %wt., Ambient pressure, 30 ml/min of hydrogen.

At low reaction temperature, the conversion of acetol was almost unchanged. This is again because 1,2-propanediol cannot dehydrated to propanaldehyde.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

The hydrodeoxygenation of acetol catalyzed by 35%wt. Ni-Cu/H-ZSM-5 and 35%wt. Ni-Cu/Al_2O_3 catalysts (bi-functional catalyst) was investigated. The Ni-Cu/H-ZSM-5 catalyst contains Ni-Cu alloy higher than that of Ni-Cu/Al_2O_3 catalyst. Moreover, the Ni-Cu/H-ZSM-5 catalyst possesses acidity higher than that of Ni-Cu/Al_2O_3 catalyst. The acid sites of Ni-Cu/H-ZSM-5 catalyst is the Bronsted acid while the Ni-Cu/Al_2O_3 catalyst contains the Lewis acid sites. It was found that the 1,2-propanediol are primarily produced by hydrogenation reaction over the Ni-Cu alloy. 1,2-Propanediol can be further dehydrated over the acid sites of the catalyst forming secondary products namely propanaldehyde and acetone. Propanaldehyde and acetone were rapidly hydrogenated presumably by hydrogen spill over to form 1-propanol and 2-propanol, respectively. In addition, higher molecular weight compounds and coke were produced from aldol condensation of propanaldehyde and acetone that is the cause of catalysts deactivation. Dehydrogenation of 1,2-propanediol to acetol over the metal sites could also be expected unless it dehydrate to propanaldehyde. It is clear that the Ni-Cu/H-ZSM-5 catalyst is more active than Ni-Cu/Al_2O_3 catalyst. Moreover, the acidity and acid type of the catalysts affect to the yield of the desired product. The Ni-Cu/H-ZSM-5 catalyst selectively gives 1-propanol as product while the Ni-Cu/Al_2O_3 is selective for 2-propanol. At low reaction temperature (175 °C), 1,2-propanediol cannot be dehydrated to propanaldehyde and hence 1-propanol was not obtained. This is because the E_a of dehydration reaction is relatively high while, at the high reaction temperature (225 °C), 1-propanol is highly produced. However, the catalyst was rapidly deactivated due to the formation of high molecular weight products by aldol condensation.

5.2 Suggestions for Future Studies

5.2.1) The difference zeolites and Si/Al ratio should be studied to understand the effect of pore size and the catalyst acidity.

5.2.2) It is interesting to use glycerol as feed directly that is the by-product from biodiesel process.

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APPENDICES

APPENDIX A

Elemental analysis by X-ray fluorescence

Table A1 Elemental composition of 35%wt. Ni-Cu/HZSM-5 catalyst

Al_2O_3	SiO_2	NiO	CuO	Compton	Rayleigh	Norm.
0.7 KCps	25.9 KCps	490.4 KCps	449.3 KCps			
1.39%	45.20%	29.50%	23.80%	0.9	1.1	100.00%

Table A2 Elemental composition of 35%wt. Ni-Cu/Al_2O_3 catalyst

Al_2O_3	NiO	CuO	Compton	Rayleigh	Norm.
13.9 KCps	490.1 KCps	447.9 KCps			
33.50%	36.80%	29.60%	0.83	1.08	100.00%

Example of elemental composition calculation from **Table A1**

Mole of each compositions :

Al_2O_3 = 1.39 g / (101.960 g/mol) = 0.0136 mol

SiO_2 = 45.20 g / (60.080 g/mol) = 0.7520 mol

NiO = 29.50 g / (74.690 g/mol) = 0.3950 mol

CuO = 23.80 g / (79.545 g/mol) = 0.2990 mol

Weight of each elementals :

Si = 0.7520 mol × (28 g/mol) = 21.0560 g

Al = 0.0136 mol × (2 × 27 g/mol) = 0.7344 g

Ni = 0.3950 mol × (58.69 g/mol) = 23.1800 g

Cu = 0.299 mol × (63.55 g/mol) = 19.0000 g

Si/Al ratio of H-ZSM-5 support :

Si/Al = 0.752 mol / (0.0136 mol × 2) = 27.6

APPENDIX B

Surface area analysis

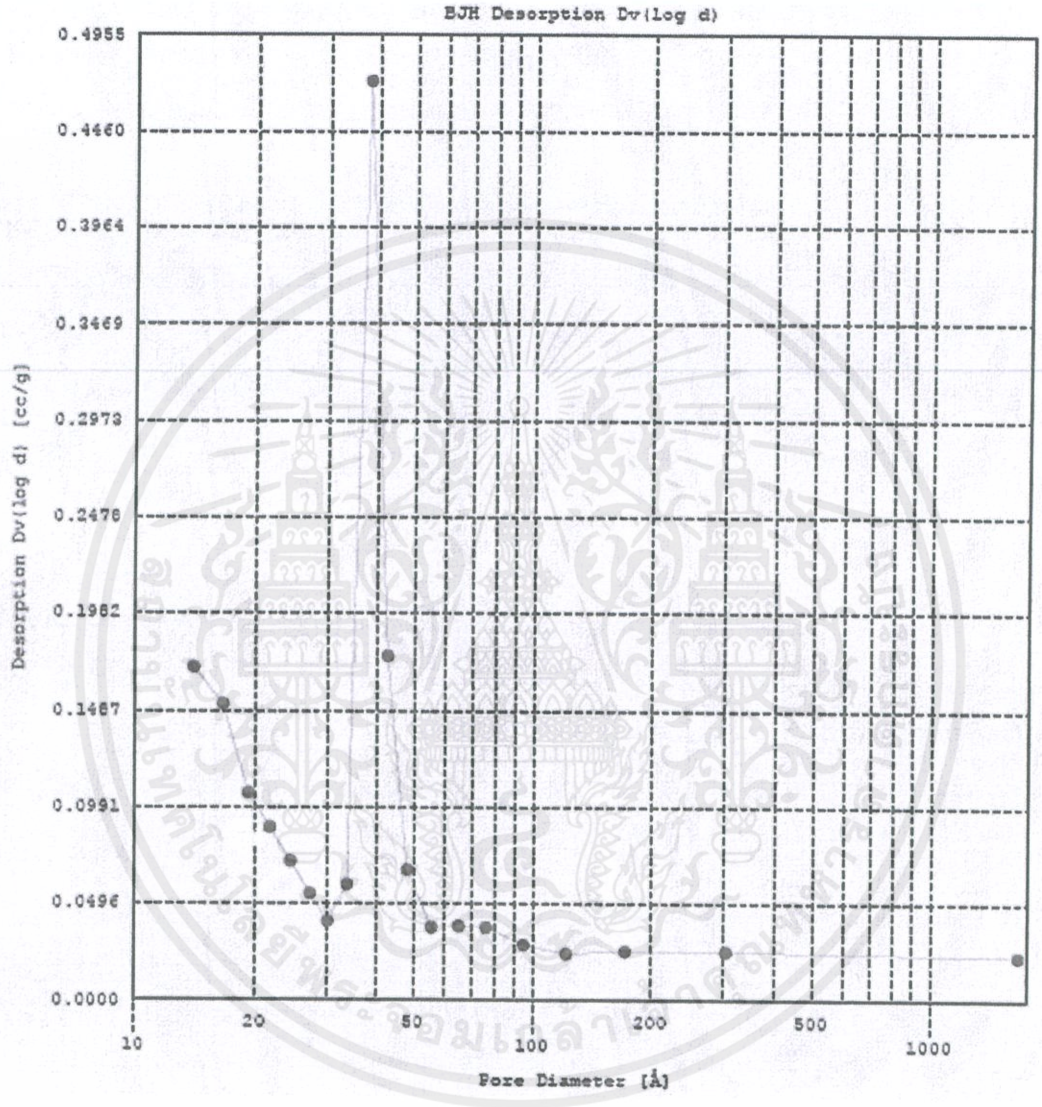


Figure B1 Pore size distribution of 35%wt. Ni-Cu/H-ZSM-5 catalyst

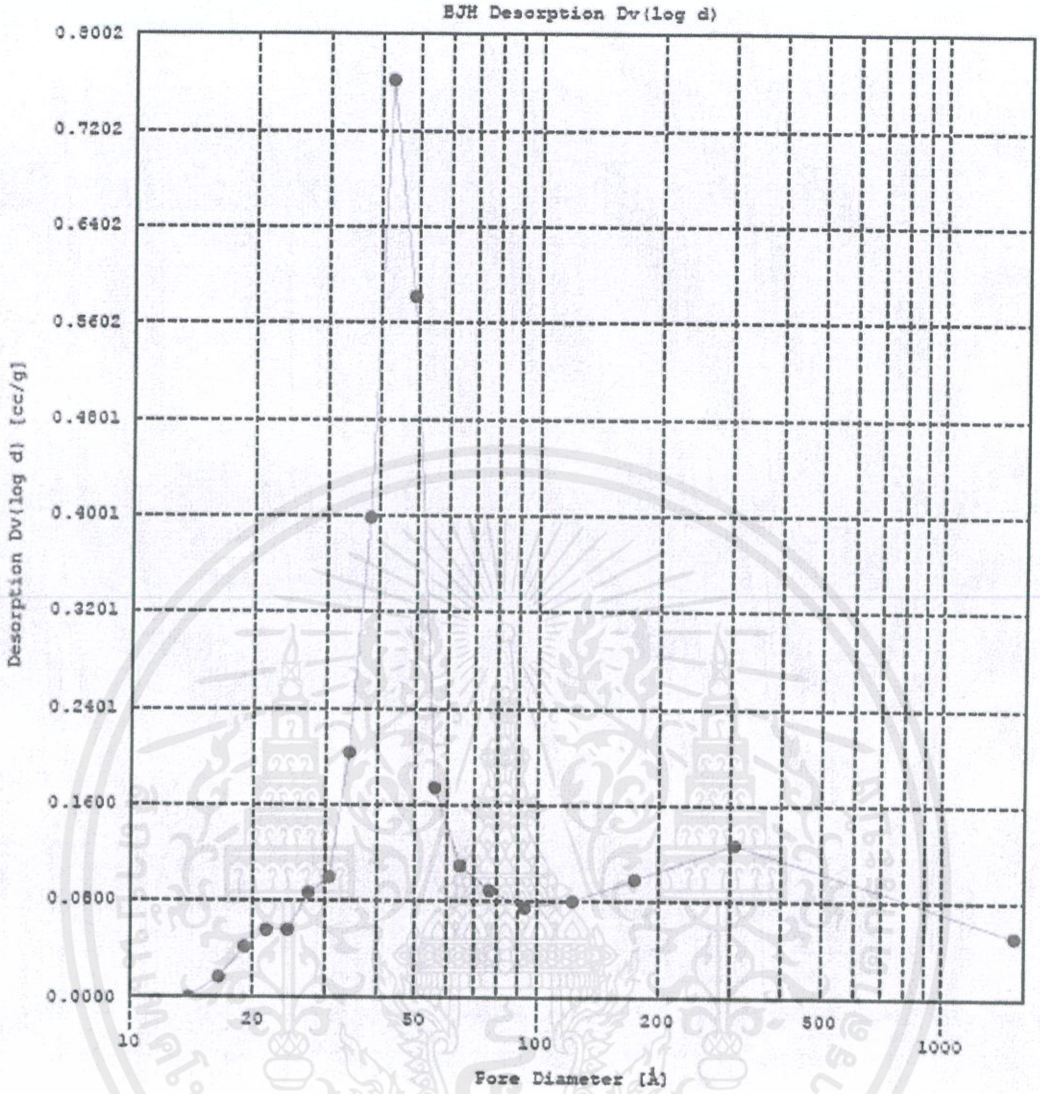


Figure B2 Pore size distribution of 35%wt. Ni-Cu/Al_2O_3 catalyst

APPENDIX C

Thermogravimetric analysis of catalysts

** Test condition; in nitrogen from 50 to 900 °C (10 °C/min)*

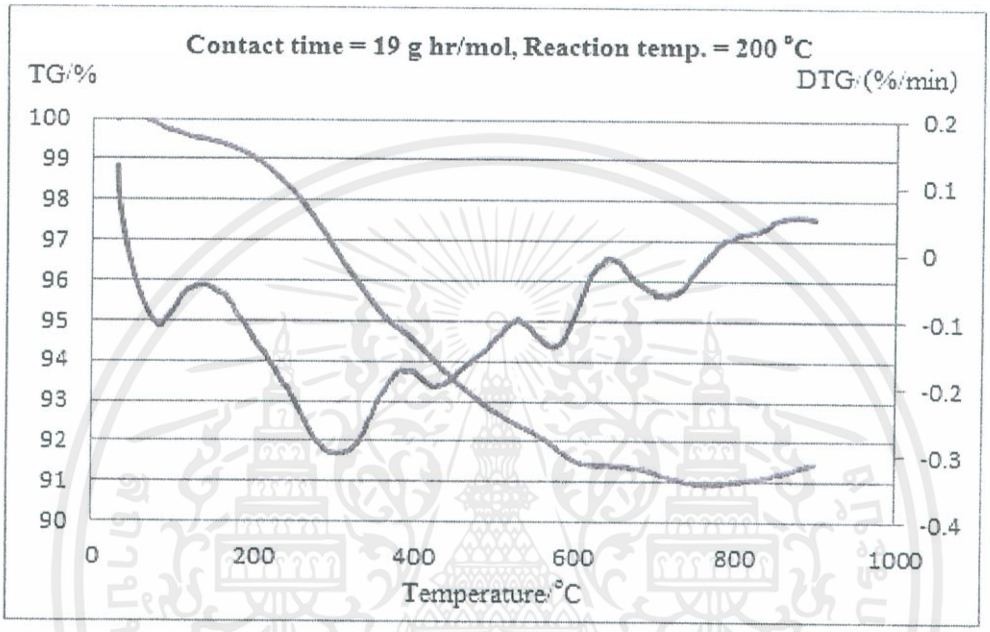


Figure C1 TGA of spent 35%wt. Ni-Cu/H-ZSM-5 catalyst at contact time of 19 g.h/mol, reaction temperature 200 °C; result shown in **Table 4.2**

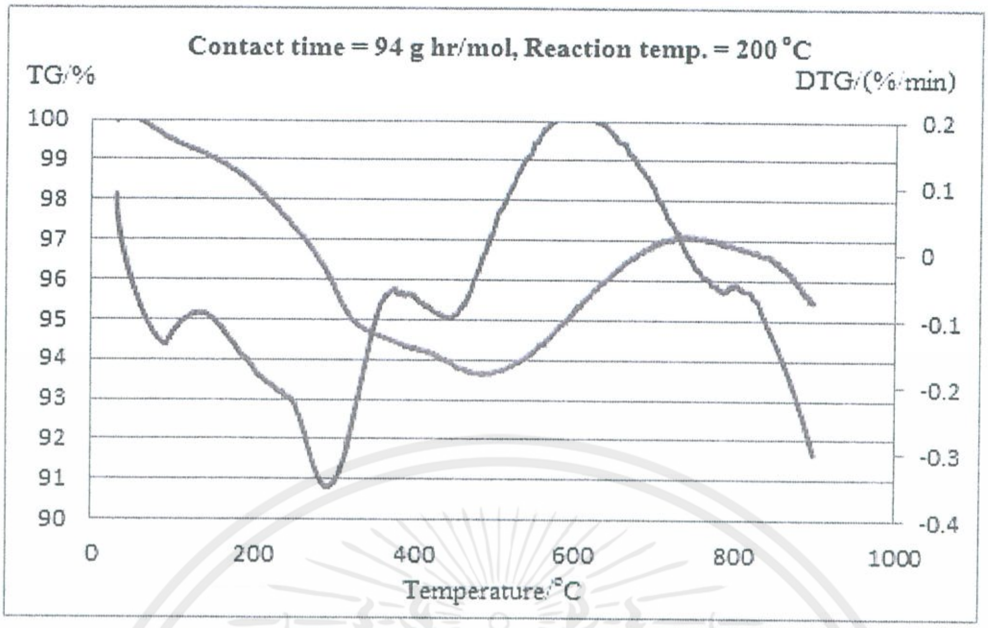


Figure C2 TGA of spent 35%wt. Ni-Cu/H-ZSM-5 catalyst at contact time 94 g.h/mol, reaction temperature 200 °C; result shown in **Table 4.2**

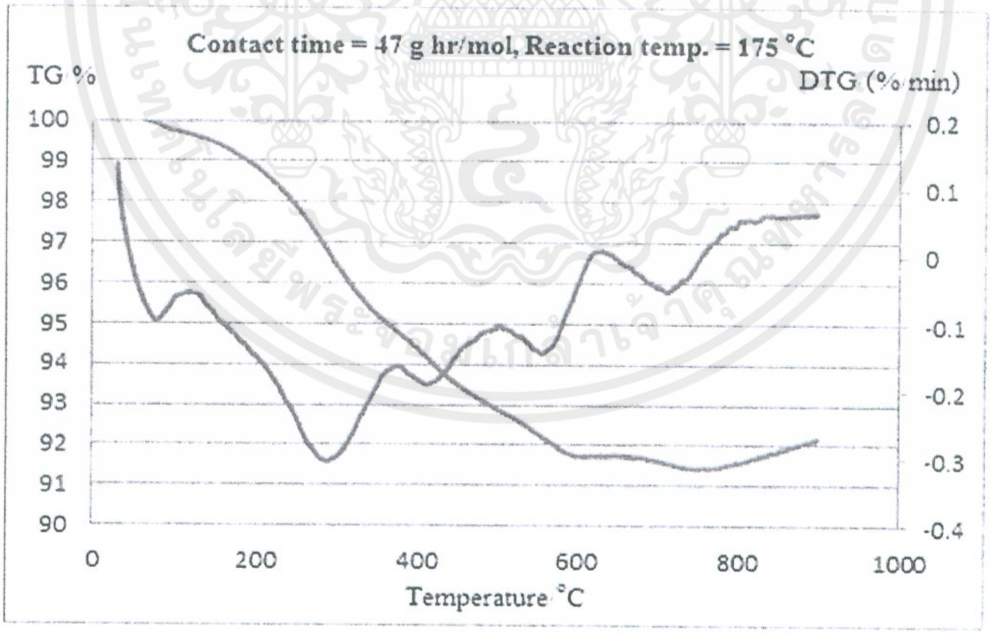


Figure C3 TGA of spent 35%wt. Ni-Cu/H-ZSM-5 catalyst at contact time 47 g.h/mol, reaction temperature 175 °C; result shown in **Table 4.2**

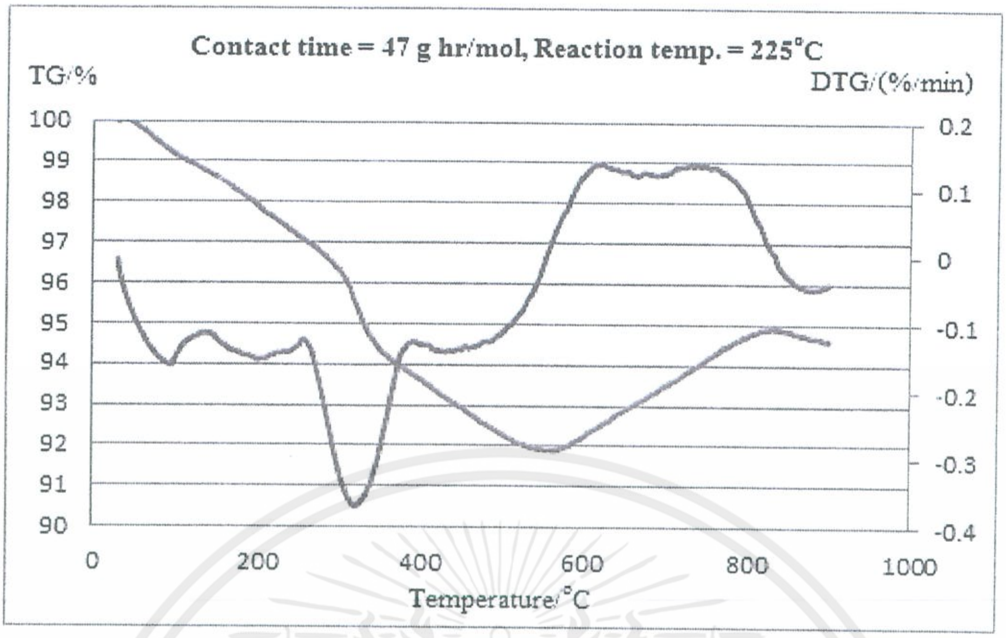


Figure C4 TGA of spent 35%wt. Ni-Cu/H-ZSM-5 catalyst at contact time 47 g.h/mol, reaction temperature 225 °C; result shown in **Table 4.2**

APPENDIX D

Reaction Data

D1 : Acetol hydrogeoxygenation over 35%wt. Ni-Cu/H-ZSM-5

D1.1 Effect of Contact time

Table D1 Product distribution from the reaction of acetol over 35%wt. Ni-Cu/H-ZSM-5 catalyst at various contact times.

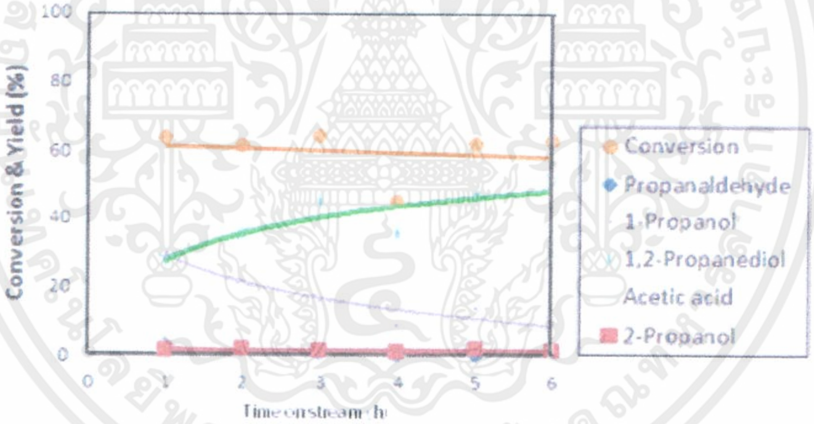
Contact time (g.h/mol)	19	47	75	94
Conversion of acetol (%)	35	64	96	98
Product yield (%)				
Acetaldehyde	0	0	0	0
Acetone	0	0	0	2
Acetic acid	0	3	0	0
1-Propanol	0	30	81	81
2-Propanol	0	1	2	2
Propanaldehyde	0	3	8	5
1,2-Propanediol	35	27	5	8

Reaction conditions; Catalyst: 35%wt. Ni-Cu/H-ZSM-5, Temperature: 200 °C, Ambient pressure, 30 ml/min of hydrogen.

Table D2 The yield of acetol hydrodeoxygenation at contact time = 19 g.h/mol

Time on stream (h)	Conversion (%)	Yield of 1,2-propanediol (%)
1	34.5	34.5
2	30.1	30.1
3	42.8	42.8
4	46.3	46.3
5	40.4	40.4
6	43.7	43.7

Reaction conditions; Catalyst: 35%wt. Ni-Cu/H-ZSM-5 0.08 g, Temperature: 200 °C, Feed: 1.575 g/h of acetol at 20 %wt., Ambient pressure, 30 ml/min of hydrogen.



Reaction conditions; Catalyst: 35%wt. Ni-Cu/H-ZSM-5 0.10 g, Temperature: 200 °C, Feed: 1.575 g/h of acetol at 10 %wt., Ambient pressure, 30 ml/min of hydrogen.

Figure D1 The acetol conversion over 35%wt. Ni-Cu/H-ZSM-5 catalyst as a function of time on stream at contact time = 47 g.h/mol.

Table D3 The yield of acetol hydrodeoxygenation at contact time = 47 g.h/mol

Time on stream	Conversion	Yield (%)				
(h)	(%)	Propanaldehyde	Acetic acid	2-propanol	1-propanol	1,2-Propanediol
1	63.7	2.5	2.6	1.3	30.0	27.4
2	61.6	1.6	1.4	1.6	21.8	35.2
3	64.2	1.1	0.9	1.5	16.0	44.7
4	44.9	0	0	1.0	8.7	35.2
5	62.0	0	0	1.8	13.7	46.6
6	62.7	0.7	0	1.3	9.4	51.3

Reaction conditions; Catalyst: 35%wt. Ni-Cu/H-ZSM-5 0.10 g, Temperature: 200 °C,

Feed: 1.575 g/h of acetol at 10 %wt., Ambient pressure, 30 ml/min of hydrogen.

Table D4 The yield of acetol hydrodeoxygenation at contact time = 75 g.h/mol

Time on stream	Conversion	Yield (%)				
(h)	(%)	Propanaldehyde	Acetone	2-propanol	1-propanol	1,2-Propanediol
1	95.8	7.6	0	2.1	81.2	4.9
2	90.6	4.8	0	2.1	63.0	20.8
3	87.7	3.5	0	2.1	48.4	33.8
4	74.9	0.5	0.3	0.3	63.5	10.2
5	82.3	2.8	0	1.9	34.2	43.4
6	81.4	2.7	4.0	1.7	31.2	41.8

Reaction conditions; Catalyst: 35%wt. Ni-Cu/H-ZSM-5 0.08 g, Temperature: 200 °C,

Feed: 1.575 g/h of acetol at 7 %wt., Ambient pressure, 30 ml/min of hydrogen.

Table D5 The yield of acetol hydrodeoxygenation at contact time = 94 g.h/mol (Ni-Cu/H-ZSM-5)

Time on stream (h)	Conversion (%)	Yield (%)				
		Propanaldehyde	Acetone	2-propanol	1-propanol	1,2-Propanediol
1	98.3	5.3	1.6	2.2	81.1	8.1
2	93.3	3.2	0	2.2	54.4	33.4
3	91.8	2.4	0	2.5	491	37.9
4	86.9	1.5	0	1.4	21.2	62.9
5	81.1	1.1	0	0.9	12.6	66.5
6	79.2	0	0	0	5.2	73.9

Reaction conditions; Catalyst: 35%wt. Ni-Cu/H-ZSM-5 0.14 g, Temperature: 200 °C,

Feed: 1.575 g/h of acetol at 7 %wt., Ambient pressure, 30 ml/min of hydrogen.

D1.2 Effect of Reaction Temperature

Table D6 Product distribution from reaction of acetol over 35%wt. Ni-Cu/H-ZSM-5 catalyst at various reaction temperatures.

Reaction temperature (°C)	175	200	225
Contact time (g.h/mol)	47	47	47
Conversion of acetol (%)	22	64	98
Product yield (%)			
Acetaldehyde	0	0	1
Acetone	0	0	1
Acetic acid	6	3	0
1-Propanol	0	30	79
2-Propanol	0	1	10
Propanaldehyde	0	3	4
1,2-Propanediol	16	27	3

Reaction condition; Catalyst: 35%wt. Ni-Cu/H-ZSM-5, Temperature: 175-225 °C,

Contact time: 47 g.h/mol, Ambient pressure, 30 ml/min of hydrogen.

Table D7 The yield of acetol hydrodeoxygenation at 175 °C

Time on stream	Conversion	Yield (%)				
(h)	(%)	Propanaldehyde	Acetic acid	2-propanol	1-propanol	1,2-Propanediol
1	58.1	2.2	13.7	0	2.5	39.8
2	57.0	0	1.3	0	1.6	54.1
3	59.7	0	0	0	0	59.7
4	65.9	0	0	0	3.2	62.7
5	55.9	0	0	0	0	55.9

Reaction conditions; Catalyst: 35%wt. Ni-Cu/H-ZSM-5 0.10 g, Contact time: 47 g.h/mol,

Feed: 1.575 g/h of acetol at 10 %wt., Ambient pressure, 30 ml/min of hydrogen.

Table D8 The yield of acetol hydrodeoxygenation at 200 °C

Time on stream	Conversion	Yield (%)				
(h)	(%)	Propanaldehyde	Acetic acid	2-propanol	1-propanol	1,2-Propanediol
1	63.7	2.5	2.6	1.3	30.0	27.4
2	61.6	1.6	1.4	1.6	21.8	35.2
3	64.2	1.1	0.9	1.5	16.0	44.7
4	44.9	0	0	1.0	8.7	35.2
5	62.0	0	0	1.8	13.7	46.6
6	62.7	0.7	0	1.3	9.4	51.3

Reaction conditions; Catalyst: 35%wt. Ni-Cu/H-ZSM-5 0.10 g, Contact time: 47 g.h/mol,

Feed: 1.575 g/h of acetol at 10 %wt., Ambient pressure, 30 ml/min of hydrogen.

Table D9 The yield of acetol hydrodeoxygenation at 225 °C

Time on stream	Conversion	Yield (%)					
(h)	(%)	Acetaldehyde	Propannaldehyde	Acetone	2-Propanol	1-Propanol	1,2-Propanediol
1	98.0	0.8	4.2	1.3	9.9	79.1	2.7
2	90.8	1.1	3.6	0.9	9.8	69.0	3.5
3	81.5	0.9	2.90	0	7.2	47.3	23.3
4	85.4	0	2.03	0	5.4	32.0	45.9
5	73.3	1.2	1.8	0	5.8	27.4	37.1
6	67.4	0.9	1.3	0	4.5	20.4	40.2

Reaction conditions; Catalyst: 35%wt. Ni-Cu/H-ZSM-5 0.10 g, Contact time: 47 g.h/mol,

Feed: 1.575 g/h of acetol at 10 %wt., Ambient pressure, 30 ml/min of hydrogen.

D2 : Acetol hydrogeoxygenation over 35%wt.Ni-Cu/Al_2O_3 catalyst

Table D10 The yield of acetol hydrodeoxygenation at contact time = 94 g.h/mol (Ni-Cu/Al_2O_3)

Time on stream	Conversion	Yield (%)	
(h)	(%)	2-propanol	1,2-Propanediol
1	85.7	12.7	73.0
2	87.1	9.8	77.3
3	86.0	11.4	74.6
4	86.2	8.0	78.2
5	84.3	9.3	75.0
6	83.3	6.6	76.7

Reaction conditions ; Catalyst: 35%wt. Ni-Cu/Al_2O_3 0.14 g, Temperature: 200 °C,

Feed: 1.575 g/h of acetol at 7 %wt., Ambient pressure, 30 ml/min of hydrogen.

D3 : 1,2-Prapanediol reaction over 35%wt.Ni-Cu/H-ZSM-5 and 35%wt. Ni-Cu/Al_2O_3 catalysts

Table D11 The yield of 1,2-propanediol reaction at contact time = 47 g.h/mol, run at 200 °C (Ni-Cu/H-ZSM-5)

Time on stream	Conversion	Yield (%)		
(h)	(%)	Propanaldehyde	Acetol	1-propanol
1	62.1	5.4	0	56.7
2	21.0	1.5	0.4	19.0
3	44.1	1.6	8.6	33.9
4	37.0	1.2	12.1	23.6
5	21.0	0	5.6	15.4
6	22.4	0.6	8.9	12.9

Reaction conditions ; Catalyst: 35%wt. Ni-Cu/H-ZSM-5 0.10 g, Temperature: 200 °C, Feed: 1.575 g/h of 1,2-propanediol at 10.25 %wt., Ambient pressure, 30 ml/min of hydrogen.

Table D12 The yield of 1,2-propanediol reaction at contact time = 47 g.h/mol, run at 200 °C (Ni-Cu/Al_2O_3)

Time on stream	Conversion	Yield (%)		
(h)	(%)	Acetone	Acetol	2-propanol
1	16.8	0	11.8	5.0
2	14.7	0	10.5	4.2
3	5.5	0.8	3.7	1.0
4	9.2	0	6.2	3.1
5	9.2	0	7.8	1.4
6	10.6	0	9.2	1.4

Reaction conditions ; Catalyst: 35%wt. Ni-Cu/Al_2O_3 0.10 g, Temperature: 200 °C, Feed: 1.575 g/h of 1,2-propanediol at 10.25 %wt., Ambient pressure, 30 ml/min of hydrogen.

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