

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Catalytic Dehydration of Bio-ethanol to Non-aromatic Hydrocarbons

Nowadays, it is well known that bio-ethanol or fermentative ethanol, which is derived from bio-mass such as sugarcanes, corn or cassava, can be used as feedstock for catalytic dehydration reaction to convert ethanol to hydrocarbons, such as ethylene, diethyl ether, oligomers, olefins, paraffins and BTX.

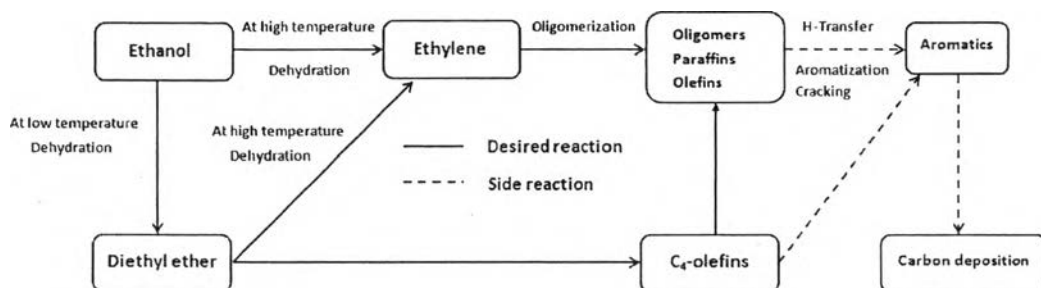


Figure 2.1 Selected pathways of ethanol transformation to larger hydrocarbons (Adapted from Wei *et al.*, 2012).

Generally, the catalytic dehydration of ethanol can take place with consecutive reactions. The first reactions take place at a low temperature, between 150 and 300°C, to form diethyl ether, and another reaction can take place at a high temperature, between 300 and 600°C, to form ethylene. Moreover, diethyl ether can undergo dehydration reaction to form ethylene at a temperature between 300 and 600°C. Furthermore, ethylene, formed by dehydration, can be converted to oligomers through oligomerization reaction which can take place through acid- or metal-catalyzed reactions. Moreover, diethyl ether, formed by dehydration, can be converted to C₄-olefins at a high temperature, and then react with other C₄-olefins to form oligomers. Additionally, both oligomers and C₄-olefins can undergo further side reactions, such as hydrogen transfer, aromatization, or cracking, to form olefins, paraffins, and aromatic hydrocarbons. If the targeted products are non-aromatics, the

desired reaction pathway of ethanol dehydration to hydrocarbons is shown in Figure 2.1. Moreover, large hydrocarbons, especially aromatics, can undergo carbonization that leads to coke formation. Other products, which are carbon dioxide, methane, acetaldehyde, ethyl acetate, and hydrogen, can be formed by the side reactions (Tsodikov *et al.*, 2008). However, the important factors that determine the activity and selectivity of products are catalyst acidity, pore size, and the presence of heteroatom in catalyst. The other reaction parameters such as temperature, space velocity, and feed composition also have the significant effect on activity and selectivity as well.

2.2 Catalysts for Catalytic Dehydration of Bio-ethanol

At present, zeolites are the most popular group of solid acid catalysts employed in the catalytic dehydration of ethanol. Researchers discovered that zeolite catalysts were better than solid oxide catalysts due to the requirement of a lower reaction temperature. These zeolites include HZSM-5, H-mordenite, H-Beta and HY. Among these zeolite catalysts, HZSM-5 is the most popular one used for the catalytic dehydration of ethanol, but it has some disadvantages because there is a large amount of aromatic hydrocarbons in the product mixtures. The reason why HZSM-5 can provide aromatic hydrocarbon products was proposed by Jae *et al.*, (2011). They mentioned that it depended on both physical and chemical properties of HZSM-5. The structure of HZSM-5, which has three-dimensional, 10-membered rings containing straight and zigzag pore channel with approximately 5.5 Å pore diameter, leads to high shape selectivity to aromatic hydrocarbons, such as benzene, toluene, and xylenes. Furthermore, its strong surface acidity also stimulated aromatization, H-transfer, or cracking reaction. In addition, the result of Viswanadham *et al.*, (2012), in the catalytic dehydration of ethanol to gasoline over nano crystalline HZSM-5, can confirm that the majority of liquid hydrocarbon products, at a 500°C, consisted of 50.6 % aromatics, followed by iso-paraffins and a trace amount of paraffins and other hydrocarbons such as ethylene, propylene. Moreover, they also found the relationship between aromatization and hydrogen

transfer, and suggested that the aromatic products increased along with the decrease of olefins and the increase of paraffins.

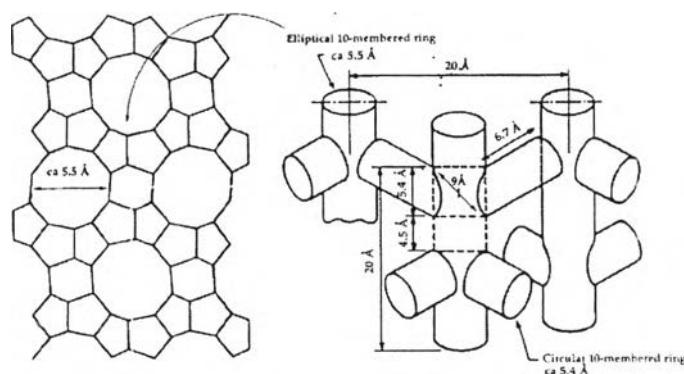


Figure 2.2 Structure of HZSM-5 zeolite (Turro *et al.*, 2003).

In order to avoid aromatics formation, γ - Al_2O_3 is one of alternative catalysts for the catalytic dehydration of ethanol to produce ethylene without containing aromatics due to it has low acidity and large pore sizes. Many research works related to ethylene production by using γ - Al_2O_3 were published, but the reaction required a high reaction temperature (450°C) and offered low ethylene yield (80%). Kagymanova *et al.*, (2011) studied the kinetic model of bio-ethanol conversion to ethylene over an alumina-based catalyst. Their experiment was set up at atmospheric pressure, the reaction temperatures in the range of 350 - 450°C , and the majority of obtained products were ethylene, diethyl ether and butylene. Furthermore, Zhang *et al.*, (2008) studied four catalysts; that are, Al_2O_3 , SAPO-11, SAPO-34, and Ni-modified SAPO-43 in ethylene production from the catalytic dehydration of ethanol. Their result showed that using γ -alumina at 450°C , the product consisted of 78.7% ethylene, 14.4% ethanol, 6.9% diethyl ether, and 0.1% acetaldehyde. The result of Aida *et al.*, (1981) showed that an activated alumina catalyst, which has 99.6% purity or more and contains a trace amount of contaminants, exhibited high activity, selectivity for ethylene, and high ethanol conversion in the catalytic dehydration of bio-ethanol at 370°C . In addition, Chen *et al.*, (2007a) studied the dehydration of bio-ethanol over TiO_2/γ - Al_2O_3 . They found that when 93.8 wt% of ethanol was used

as feedstock, 10 wt% $\text{TiO}_2/\gamma\text{-Al}_2\text{O}_3$ gave a high ethanol conversion of 99.7% and ethylene selectivity of 98.6%.

2.3 Oligomerization of Ethylene

In order to produce oligomer products through the oligomerization of ethylene produced from the catalytic dehydration of bio-ethanol, actually, the reaction does not need only acid catalyst, but also needs a metal catalyst to initiate. So, a metal-promoted catalyst can play an important role in this reaction. Moreover, there are many involved reactions, such as insertion, isomerization, and dimerization, that can be occurred. The reaction pathway of ethylene oligomerization by using Ni-supported AlMCM-41 catalysts was proposed by Hulea and Falula (2004)

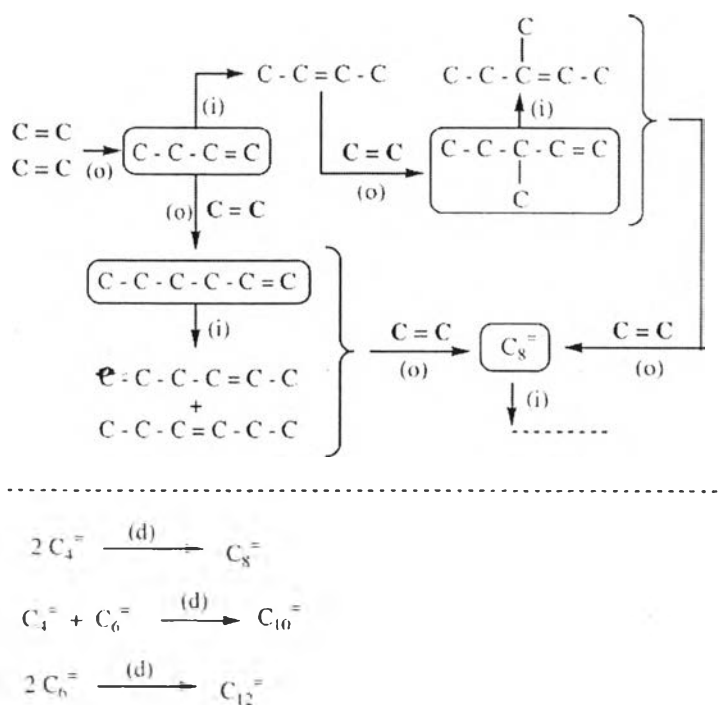


Figure 2.3 Ethylene oligomerization pathway using Ni/Al-MCM-41 (Hulea and Falula, 2004).

Typically, ethylene oligomerization can be occurred when ethylene molecule is initiated over metal sites on an acid catalyst to form a carbenium ion, and

then reacts with other ethylene molecules to form C₄-olefins, especially 1-butene. Furthermore, these C₄-olefins can undergo further reaction, such as insertion, oligomerization, and double bond isomerization, to form larger olefin hydrocarbons. These subsequent reactions can be occurred on both metal sites and weak acid sites even at a moderate to high temperature. Moreover, in the case of catalysts that have strong acidity or high acid site concentrations, unsaturated aliphatic C₄ and C₆ hydrocarbons can undergo dimerization reaction, via carbenium ion mechanism, to form branched chain oligomerized products. Furthermore, important parameters that influence the reactions are acidity, pore size, temperature, pressure and the presence of heteroatom on catalysts.

2.4 Metal Catalysts for Fisher-Tropsch Process

Fischer-Tropsch reaction is a chemical reaction to convert the mixture of carbon monoxide and hydrogen to hydrocarbon products in the range of gasoline to wax. The conversion of carbon monoxide to alkanes involves hydrogenation, hydrogenolysis, and formation of alkanes. Typically, these reactions are catalyzed by using cobalt or iron-based catalysts to produce hydrocarbons products, which are composed of diesels, paraffins, lubricants, and waxes. The hydrocarbon chain growth, which occurs in Fischer-Tropsch synthesis, relates to the re-adsorption of alkyl group on metal sites, and then chain termination leads to the formation of large hydrocarbons in the range of C₄-C₂₀ hydrocarbons products (Iglesia, 1997).

2.4.1 Cobalt Catalysts

Cobalt is classified as a transition metal with high availability. The application of cobalt in catalytic fields, such as Fischer-Tropsch synthesis, is to produce long-chain hydrocarbons. Moreover, cobalt-based catalysts are considered to be the most efficient in Fischer-Tropsch synthesis because their high activity, better stability, high selectivity for long-chain hydrocarbon and resistance to water attraction (van Steen and Claeys, 2008). Iglesia (1997) mentioned that C₅₊ selectivity increased with increased cobalt site density because the re-adsorption of α -olefins led to initiation of alkyl surface chains and then large hydrocarbon formation. Bechara *et*

al., (2001) studied Co/Al₂O₃ catalysts for hydrocarbon synthesis. They found that the increasing catalyst activity related to the increase in the reduction temperature and the amount of Co sites. Moreover, both of them were causes of the increasing transformation rate and high site density, respectively. Furthermore, they also found that, using Co/Al₂O₃, the obtained products were in the range of gasoline to wax. Cobalt-supported ZSM-5 catalysts for producing gasoline-range hydrocarbons via Fischer-Tropsch synthesis was studied by Kang *et al.*, (2011). They revealed that the enhancement of C₂-C₉ hydrocarbons selectivity on the catalysts was attributed to the presence of large pore size with the increased product transport. Furthermore, Braganca *et al.*, (2012) studied Co-Fe bimetallic nanocrystals deposited on SBA-15 and HMS mesoporous silica catalysts for Fischer-Tropsch synthesis. They revealed that cobalt over the mesoporous supports exhibited high C₅₊ selectivities. Wang *et al.*, (2013) studied gasoline production from Fischer-Tropsch synthesis over Ru-, and Ni-promoted Co/HZSM-5 catalysts. They found that products, in the oil phase, consisted of olefins, paraffins, iso-paraffins, and a small amount of cycloparaffins, but aromatic hydrocarbons were not detected. The selectivity for gasoline-range hydrocarbons reached the maximum value of 57.8% at 540 K for Co/HZSM-5. However, Cant *et al.*, (2013) studied ethylene oligomerization over Co/SiO₂. They found that more than 50% yield of large hydrocarbons were produced. The obtained products, which was aliphatic hydrocarbons included butenes, n-butane, C₃, C₅, C₆. Especially cis-2-butene is dominated amongst the formed oligomer products.

Therefore, from these previous reviews of research work, it can be concluded that cobalt catalysts can be used to produce olefins and paraffins, and the products mostly consisted of C₄-C₁₈ hydrocarbons. However, the formation of olefins and paraffins was attributed to the amount of cobalt metallic sites formation on the catalysts.

2.4.2 Iron Catalysts

An iron catalyst is commonly used in Fischer-Tropsch synthesis to produce hydrocarbon products. Many researchers studied about iron catalysts in this area. O'Brien *et al.*, (1997) studied the activity and selectivity of precipitated iron catalysts in Fischer-Tropsch synthesis. They revealed that iron catalysts, at a

temperature of 230°C, gave aliphatic C₂-C₁₁ hydrocarbon selectivity more than 75%, and C₁₂₊ hydrocarbons selectivity more than 70%. Moreover, O'Shea *et al.*, (2007) studied Fischer-Tropsch synthesis by using monometallic Co and Fe catalysts in a fixed-bed and a slurry reactor. They found that Fe catalysts had higher light hydrocarbon selectivity than Co catalysts, but long-chain hydrocarbon production was lower than that from the Co catalysts. Moreover, they concluded that the formation of light hydrocarbons was a behavior of Fe catalysts. Furthermore, Fe and Fe-supported ZSM-5 catalysts for Fischer-Tropsch synthesis were studied by Pour *et al.*, (2008). They revealed that the Fe-supported ZSM-5 catalysts provided long chain of hydrocarbons higher than unsupported Fe catalysts because Fe-supported ZSM-5 catalysts enhanced the secondary chain growth reaction. Kang *et al.*, (2010) studied Fe catalyst supported on ZSM-5 zeolite in Fischer-Tropsch process in order to produce light olefins. They revealed that the metallic iron and iron carbide (FeC_x) were active phases for Fischer-Tropsch reaction. Moreover, they also found that Si/Al ratio played an important role on Fischer-Tropsch reaction; that is, the increasing Si/Al ratio resulted in the reduction of activity and selectivity in Fischer-Tropsch reaction. In addition, kerosene production in Fischer-Tropsch synthesis was studied by Kumabe *et al.*, (2010). They found that the reduced Fe preferred to produce olefins than paraffins in C₆₊ hydrocarbon range. Moreover, their result also showed low chain growth and low paraffins produced by hydrogenation of olefins due to low surface area of Fe. However, Yoneyama *et al.*, (2005) studied Fe-based catalysts over HZSM-5 zeolite in Fischer-Tropsch. They found that n-paraffins and α-olefins were produced through Fe-catalyzed Fischer-Tropsch reaction. The product distribution of hydrocarbon obtained from Fe catalysts was in the range of C₁-C₁₆ hydrocarbons. Finally, it can be concluded that Fe catalysts can be used to produce short-chain hydrocarbons and iso-paraffins. The products consisted of C₄-C₆ hydrocarbons with the number of branches greater than those of aliphatic hydrocarbons. However, the size of Fe also affected to the product formation.

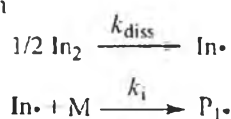
In summary, among metal catalysts for Fischer-Tropsch synthesis, both Co and Fe have the best performance in producing hydrocarbon products, but there are some differences between the two obtained products. Using cobalt catalysts, the obtained products are olefins and paraffins in the range of greater than C₄

hydrocarbons, but in the case of iron catalysts, the products are branched short-chain hydrocarbons in the range of less than C₁₀ ones.

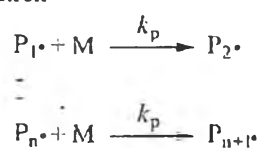
2.5 Metal Catalysts for Olefins Polymerization Reaction

Olefin polymerization is a reaction that involves the linkage of a large number of unsaturated monomers such as ethylene. The monomers must have a pi-bond in their molecules, which can break and link up with other monomers to form a repeating chain. An obtained polymer typically has a backbone containing only carbon atom. The involved mechanism can be divided into four important steps; that are, initiation, propagation, chain transfer, and termination.

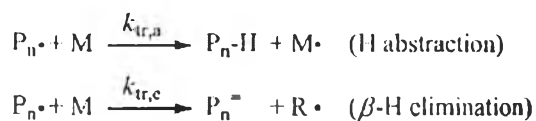
Initiation



Propagation



Chain transfer



Chain termination

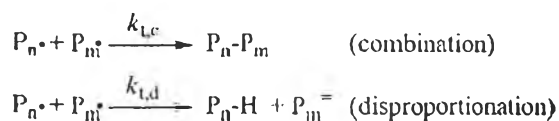


Figure 2.4 Polymerization Mechanism (Lena and Matyjaszewski, 2010).

Generally, olefin polymerization does not require high a temperature and pressure because it is difficult to control the rate of propagation and termination.

However, there is a new method to better control these two steps, which is the use of metal catalysts, Ziegler-Natta or metallocene catalysts, with co-catalysts (initiators) such as methylaluminoxane (MAO). The formed polymers with using these two types of catalysts, which are Ziegler-Natta or metallocene catalysts, have a high molecular weight. However, the reduction of molecular weight can be done by adding hydrogen gas to polymerization system.

2.5.1 Nickel-based Catalysts

Metallic nickel is widely used in various reactions such as hydrogenation, hydroisomerization, oligomerization and polymerization due to the low cost and high availability. Lallemand *et al.*, (2006) studied the catalytic oligomerization of ethylene over nickel-containing dealuminated Y catalysts. The catalysts were prepared by using ion-exchanged method. They found that nickel-loaded catalysts gave better activity to produce oligomers as the desired product at a reaction temperature of 50°C, and 35 MPa ethylene pressure. The products consisted of C₄-C₁₂ unsaturated aliphatic hydrocarbons, especially C₄ as the dominant product. Moreover, heterogeneous nickel-supported HBETA catalysts for ethylene oligomerization were proposed by Martinez *et al.*, (2013). Their results showed that Ni²⁺ species were responsible to the initiation of ethylene and the undertaking oligomerization. Moreover, they found that the amount of nickel loading responsible for the product distribution. A bifunctional catalyst, nickel over HZSM-5, in n-decane hydroisomerization was studied by Romero *et al.*, (1996). They found that the product selectivities, at a reaction temperature of 290°C, 5055 kPa hydrogen atmosphere, and n-decane as the feed, were in the range of C₃-C₁₄ hydrocarbons. Furthermore, nickel sulfate over Al₂O₃ in propene oligomerization was studied by Cai (1999). Their results showed that the product distribution, at 353 K and 2.5 MPa, and propene as a feed, was in the range of C₆-C₁₈ hydrocarbons. Additionally, nickel over MCM-41 catalysts for ethylene oligomerization was studied by Hulea *et al.*, (2004). Their results showed that C₆ hydrocarbons in oligomer product consisted of 1-hexene, 2-hexene, 3-hexene and methyl-pentenes. Additionally, nickel over a mesoporous support in the catalytic dehydration of methanol into long chain hydrocarbons was studied by Hulea *et al.*, (2013). They mentioned that the

enhancement of catalyst activity, at 150°C and 3.5 MPa ethylene pressure, was attributed to the pore diameter of supported materials, which also affected to the size of hydrocarbon products as well as the yield of products exclusively C₄-C₁₀ olefins. Thus, it can be concluded that nickel catalysts have a good performance on producing unsaturated aliphatic hydrocarbons without aromatic hydrocarbon formation, and the obtained hydrocarbons are in the range of C₄-C₁₈ carbon atoms, which 1-butene is the dominant product. However, the amount of nickel formation affected to the product distribution as well.

2.5.2 Copper-based Catalysts

Atomic Transfer Radical Polymerization (ATRP) was firstly discovered in 1995. It is used in the synthesis of polymer from a vinyl monomer such as styrene, methylacrylate, and acrylonitrile with controllable molecular weight. This polymerization system takes place through radical polymerization as similarly as ethylene polymerization. The commonly-used catalyst is in the form of copper halide such as CuBr and CuCl (Matyjaszewski and Tsarevsky, 2014). A CuBr catalyst with a branching agent, divinyl benzene, used in the ATRP polymerization in order to produce branched polystyrene was proposed by Ren *et al.*, 2006. They found that CuBr had ability to product branched polystyrene at 80°C, under atmospheric pressure, and styrene as a feed. Moreover, linear polystyrene production by using CuBr catalyst with iso-propylbenzene as chain transfer agent in atomic transfer radical polymerization was studied by Bibiao *et al.*, 2006. They found that the obtained polymer, when using styrene was feed, at a reaction temperatures 80-100°C, 1 atm, and under argon atmosphere, was linear polystyrene. Moreover, Barthelemy *et al.*, 2011 studied polystyrene production in the ATRP polymerization by using CuBr over TiO₂ substrate. Their experiments were set up at 90°C, 1 MPa, and styrene as the feed. The results showed that CuBr can initiate styrene polymerization, and the obtained product was polystyrene. Additionally, a CuCl catalyst for styrene polymerization was studied by Cheng *et al.*, 2005. Their results, at 85°C and 1 MPa, showed that CuCl can encourage styrene polymerization, and the product was polystyrene. Thus, it can be concluded that copper-based catalysts have good performance in the production of polystyrene, but the obtained product can be linear

or branched depends on the type of initiators. Typically, the synthesized polystyrene was obtained in the form of linear hydrocarbons.

2.5.3 Chromium-based Catalysts

Chromium is commonly used as a metal catalyst in polymerization reaction because it has high activity, and gives selectivity for polyethylene (Jeon *et al.*, 2014). Moreover, the results of Gaspar *et al.* (2003) from the characterization of chromium catalysts, showed that the Cr^{3+} and Cr^{2+} species were responsible for dehydrogenation and polymerization, respectively. Also, they found that the catalytic activity for dehydrogenation reaction depended on the dispersion of Cr^{3+} species, and the activity of ethylene polymerization was related to the amount of Cr^{2+} species. Furthermore, chromium catalysts catalyzed ethylene tetramerization to 1-octene was studied by Chen *et al.*, (2007b). They revealed that $\text{CrCl}_3 \cdot 3(\text{THF})$ was used as a precursor of Cr (III), and also found that the product selectivity at 55°C and 3 MPa was in the range of unsaturated C_4 - C_8 hydrocarbons, and C_6 products were methylcyclopentane and methylenecyclopentane. Shao *et al.*, (2014) studied chromium catalysts, with N-isopropyl bis(diphenylphosphino)amine (PNP) ligand, supported on NAY zeolite for ethylene tetramerization. They found that Cr catalysts, which were prepared by grafting method, had high activity, and the product selectivity, at 50°C and 2 MPa ethylene pressure, was in the range of unsaturated C_4 to polyethylene. Moreover, C_6 hydrocarbons were similar to those of Chen *et al.*, (2007b). In addition, ethylene polymerization by using chromium-supported SBA-15 catalysts was investigated by Aguado *et al.*, (2008). They found that Cr/AlSBA-15 prepared by incipient wetness impregnation exhibited high activity, and the obtained product at 90°C, under 35 bar ethylene pressure and 5 bar H_2 atmosphere, was HDPE. Calleja *et al.* (2005) studied chromium-supported Al-MCM-41 catalysts for ethylene polymerization. They found that Cr/Al-MCM-41, which was prepared by incipient wetness impregnation, gave higher ethylene polymerization activity and higher polyethylene production than conventional Cr/ SiO_2 because the large pore size and pore volume of MCM-41 support that enhanced the propagation of hydrocarbon products. The polymer obtained using this catalyst, at 85°C and 40 bar ethylene pressure, was linear high-density polyethylene (HDPE).

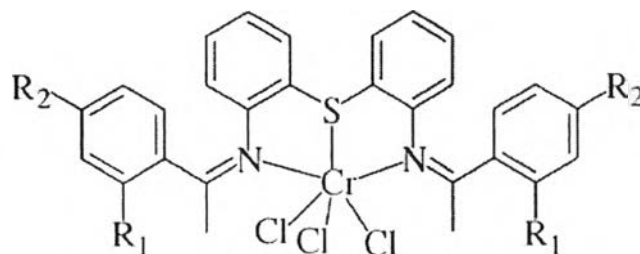


Figure 2.5 Chromium (III) complex catalyst (Liu *et al.*, 2006).

Additionally, a synthesized chromium (III) complex catalyst for ethylene polymerization was reported by Liu *et al.* (2006). They revealed that, in the catalyst preparing step, $\text{CrCl}_3 \cdot 3\text{H}_2\text{O}$ was used as a source of chromium for chromium complex catalysts, and these catalysts displayed moderate activity and produced highly linear polyethylene with broad molecular-weight distribution at 50°C and 5 atm ethylene pressures. Hence, it can be concluded that chromium catalysts have good performance to produce both saturated and unsaturated aliphatic hydrocarbons without aromatic hydrocarbon co-production, and the obtained products are in the range of unsaturated C_4 hydrocarbons to linear polyethylene.

2.5.4 Palladium-based Catalysts

Musolino *et al.*, (2010) investigated the role of group VIII transition metals, such as Pt, Pd, and Rh, in selectivity for hydrogenation or isomerization reaction of *cis*-2-butene-1,4-diol. Their results, at 303 K, and 0.1 MPa hydrogen pressure, showed that Pd/SiO₂ can promote double bond and geometric isomerization reactions, leading to the formation of 2-hydroxytetrahydrofuran, and *trans*-2-butene-1,4-diol as products. The formations of these two products are derived from isomerization and hydrogenation reactions. Moreover, selective hydrogenation of 3-hexyne over palladium catalysts was studied by Alvez-Manoli *et al.*, (2010). They found that Pd catalysts can provide hydrogenation and isomerization at 298 K, 40 psig pressure, and under hydrogen atmosphere. The dominant products were hexane and *trans*-3-hexene. Furthermore, Urzhutsev *et al.*, (2014) studied the isomerization of *n*-butane over Pd-SO₄/ZrO₂ catalysts. The authors revealed that the palladium

catalysts provided high n-butane conversion and high iso-butane selectivity (92-98%) at 155°C, under 25 bar H₂ atmosphere.

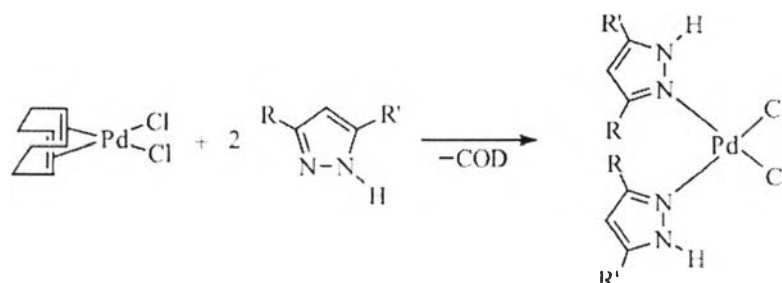


Figure 2.6 Pyrazole palladium (II) synthesis (Li *et al.*, 2002).

Additionally, Li *et al.*, (2002) studied a synthesized pyrazole palladium (II) complexes as catalysts for ethylene polymerization. The catalysts had high activity at 25-70°C and 5 atm. The obtained product was HDPE. Moreover, (pyrazol-1-yl) carbonyl palladium complex catalysts for ethylene polymerization was studied by Myoki *et al.*, (2013). They revealed that the catalysts exhibited moderate activity at 50°C, 5 bar pressure, and the obtained products was linear HDPE. Furthermore, they also found that the structure of catalysts had significant effect to catalyst activity. Hence, it can be concluded that palladium catalysts have the ability to promote isomerization and polymerization, and it can be used to produce linear HDPE.

In conclusion, metal catalysts for ethylene polymerization can be divided into two sub-groups based on the difference in the obtained product. The first group consists of nickel (Ni) and chromium (Cr). These two metal catalysts have the ability to provide products in the range of unsaturated C₄ hydrocarbons to linear long-chain hydrocarbons. However, another group consists of copper (Cu), zirconium (Zr), vanadium (V), and palladium (Pd). All of these four metals have good performance in production of linear hydrocarbons.

The production of oligomer products (C₄-C₂₀) through ethylene oligomerization in the catalytic dehydration of bio-ethanol is expected to be accomplished by incorporation of metal or metal oxide catalysts over a suitable

support, which does not provide aromatic hydrocarbons in the product mixture. So, $\gamma\text{-Al}_2\text{O}_3$ is one of alternative catalysts for ethylene production because of its properties, which are low acidity and large pore size that leads to promotion of large hydrocarbons. Moreover, ethylene oligomerization can occur through protonation of ethylene, forming a carbenium ion, which then reacts with other ethylene molecules to form larger hydrocarbons. In addition, the groups of metal catalysts, such as Fischer-Tropsch process, and olefin polymerization, have potential to produce long chain hydrocarbons, at least C_4 . Cobalt and iron are commonly used to catalyze Fischer-Tropsch process reaction, and the obtained products are aliphatic saturated hydrocarbons in the range of $\text{C}_4\text{-C}_{20}$. So, using supported Co and Fe on $\gamma\text{-Al}_2\text{O}_3$ in the catalytic dehydration of bio-ethanol might promote oligomerization of ethylene, and the obtained products are expected to be saturated hydrocarbons. Moreover, in olefin polymerization, nickel, chromium, copper and palladium commonly behaved as active sites on metal catalysts, and the obtained products are saturated and unsaturated aliphatic hydrocarbons. Thus, using supported Ni, Cu, Cr, and Pd on $\gamma\text{-Al}_2\text{O}_3$ in the catalytic dehydration of bio-ethanol might promote oligomerization of ethylene, and produce saturated and unsaturated aliphatic hydrocarbons.

In this work, the effect of metal-promoted catalysts was investigated in catalytic dehydration of bio-ethanol to study the possibility of ethylene oligomerization and the growth of ethylene from the products. In the first part, cobalt and iron on $\gamma\text{-Al}_2\text{O}_3$ were investigated, aiming to produce saturated hydrocarbons in the range of $\text{C}_4\text{-C}_{20}$. In the second part, nickel and chromium on $\gamma\text{-Al}_2\text{O}_3$ were investigated, aiming to produce aliphatic unsaturated hydrocarbons. In the third part, copper, and palladium were investigated, aiming to produce saturated hydrocarbons. The quantity of obtained products was compared with those obtained from other metal-promoted catalysts in the same part.