

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Mixed C4

Fluid Catalytic Cracking Unit (FCC) in petrochemical industry produces represent in mixed C4 containing several types of hydrocarbons mainly having 4 carbons in its molecule, such as C4-acetylenes, butadienes, butenes and butane. The three main components are 1,3-butadiene, butenes and isobutylene. The typical composition of mixed C4 from FCC unit is shown in Table 2.1.

Table 2.1 Typical hydrocarbon composition in mixed C4 from FCC unit

Compound	wt %
1,3-Butadiene	35-50
1,2-Butadiene	0-0.5
Isobutylene	20-25
Butenes	20-25
Butane	5-10
Propane/propylene	0-1
C4-Acetylenes	0.5-1.5

From table 2.1, shows the main component is 1,3-Butadiene. The composition is 35-50 wt%. The butadiene present in this mixed C4 fraction is separated by extractive distillation. Butadiene is used as monomer for making synthetic rubber (BR/SBR). Moreover, isobutylene is used to make methyl tert-butyl ether (MTBE) and 1-butene can be utilized as a co-monomer for the production of linear low density polyethylene (LLDPE). However, after extractive distillation process the raffinate stream also contains traces of butadiene and C4-acetylene stream, contains high portion of vinyl acetylene, up to 30 wt %. Vinyl acetylene is the contaminant of butadiene and 1-butene products. Thus, hydrogenation process is

used to remove vinyl acetylene from mixed C4 stream convert to high value compounds such as 1,3-Butadiene. The compositions of raffinate stream are shown in table 2.2.

Table 2.2 The composition of high concentrated vinyl acetylene mixed C4

Compound	wt %
1,3-Butadiene	10-30
1,2-Butadiene	1-5
Isobutylene	5-10
<i>n</i> -Butenes (1-Butene, 2-Butene)	40-50
Butane	2-5
Ethyl Acetylene	2-5
Vinyl Acetylene	10-30

2.2 Hydrogenation Reaction

Hydrogenation is a chemical reaction, adding pairs of hydrogen atoms to molecule alkene or alkyne. The process is commonly employed to reduce or saturate organic compounds. Catalysts are required for the reaction to provide the optimum reaction. Hydrogenation of unsaturated hydrocarbons has been utilized in many applications such as widely used in the synthesis and manufacture of fine and industrial chemical or even used to treat or purify the feeds or raw materials. The hydrogenation reaction of unsaturated hydrocarbon is shown in Fig 2.1.



Figure 2.1 Hydrogenation reaction of unsaturated hydrocarbon.

2.2.1 Hydrogenation Reaction of C4-acetylene

The C4-Acetylene hydrogenation reaction is the very complex reaction because many unsaturated compounds are involved. For example, vinyl acetylene, ethyl acetylene, 1,2-butadiene, 1,3-butadiene, cis-2-butene, trans-2-butene and 1-butene. In the first part, acetylene compound will be hydrogenated to butadiene. Then, complex reaction mechanisms occur as be shown in Fig.2.2.

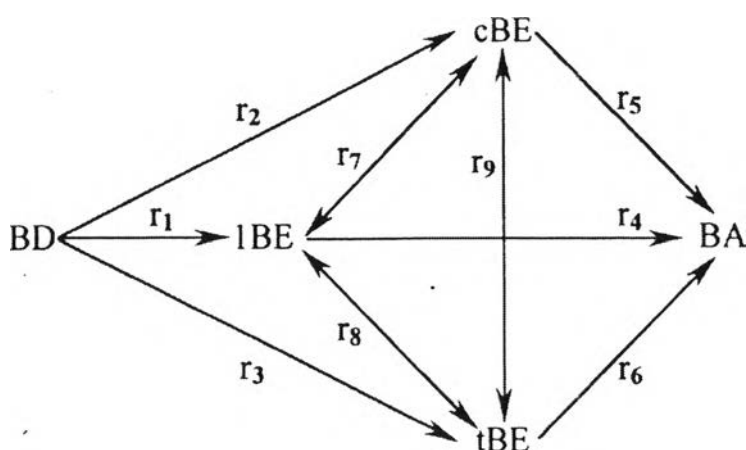


Figure 2.2 Reaction mechanism network of butadiene (Ardiaca *et al.*, 2001).

2.2.2 Hydrogenation Reaction of 1-hexyne

1-hexyne is hydrogenated to 1-hexene with a pair of hydrogen atom. Continuously, 1-hexene is hydrogenated to n-hexane as final product by another pair hydrogen atom.

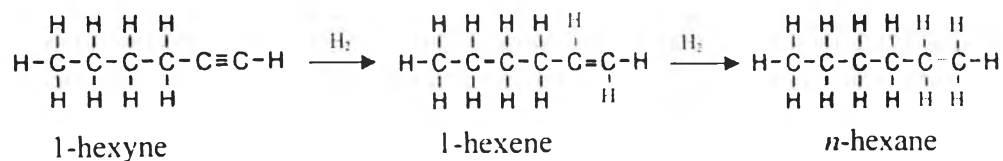


Figure 2.3 Reaction of 1-hexyne.

2.3 Catalysts

A catalyst accelerates a chemical reaction. It does so by forming bonds with the reacting molecules, and by allowing these to react to a product, which detaches from the catalyst, and leaves it unaltered such that it is available for the next reaction. In fact, we can describe the catalytic reaction as a cyclic event in which the catalyst is participated and recovered in its original form at the end of the cycle. Considering the catalytic reaction between two molecules A and B to give a product P, see Fig. 2.4. The cycle starts with the bonding of molecules A and B to the catalyst. A and B then react within this complex to give a product P, which is also bound to the catalyst. In the final step, P separates from the catalyst, thus leaving the reaction cycle in its original state.

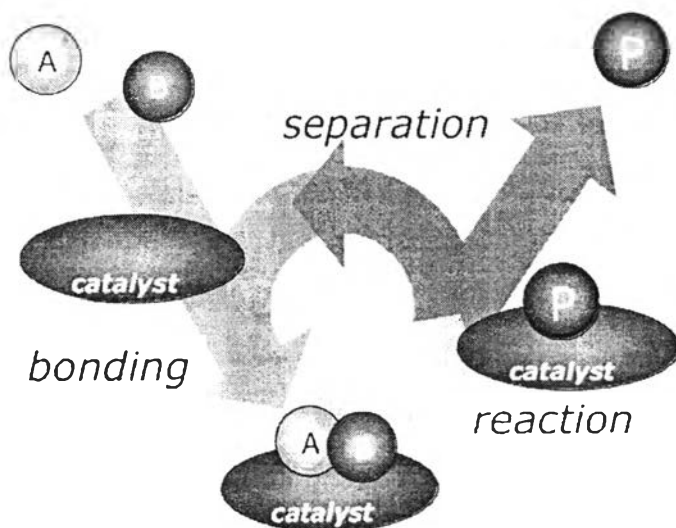


Figure 2.4 The catalytic reaction (Niemantsverdriet, 2007).

The catalytic reaction starts by bonding of the reactants A and B to the catalyst, in a spontaneous reaction. Hence, the formation of this complex is exothermic, and the free energy is lowered. There then follows the reaction between A and B while they are bound to the catalyst. This step is associated with an activation energy; however, it is significantly lower than that for the uncatalyzed reaction. Finally, the product P separates from the catalyst in an endothermic step.

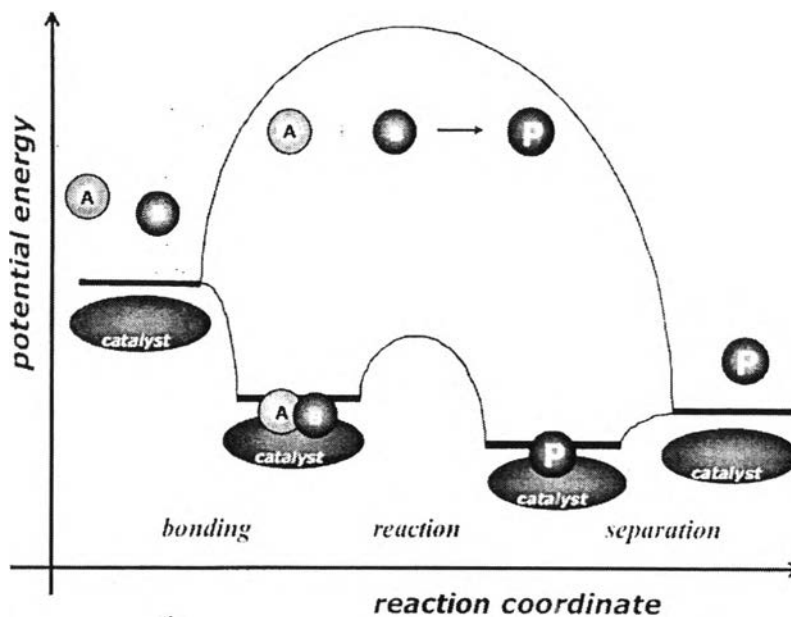


Figure 2.5 Potential energy diagram of a heterogeneous catalytic reaction (Niemantsverdriet, 2007).

2.3.1 Heterogeneous Catalysis

Heterogeneous catalysis is the form of catalysis where the phase of the catalyst differs from that of the reactants. To use the often expensive materials (e.g. palladium) in an economical way, catalysts are usually nanometer-sized particles supported on an inert porous structure. The impregnation to incipient wetness is known for preparing the catalyst. The support is doped with a solution of appropriated concentration, corresponding in quantity to the total known pore volume of the support, or slightly less. The catalyst is then usually dried and calcined. Oxide supports such as alumina is the most widely used support because it is inexpensive, structurally stable and because it can be prepared with a wide variety of pore sizes and pore size distributions. Commercial alumina materials are available with surface areas in the range of 100-600 m²/g.

2.4 Nanoparticles Catalysis Hydrogenation

Generally, heterogeneous catalysis is preferred as opposed to homogeneous since the former offers ease of handling, separation, regeneration, and thermal stability. However, because heterogeneous catalysts are not as selective as their homogeneous counterparts, nanoparticle catalysts have been introduced, due to their large surface area, in an attempt to address limitations. The challenge lies in combining the advantages of both types of catalysts either homogenizing heterogeneous catalysts or heterogenizing homogeneous catalysts through nanochemistry. Usually, nanoparticle metal catalysts are preferred for hydrogenation rather than single crystals. For efficient hydrogenation, the subsurface hydrogen formation is the key and both the nanoparticles and crystals facilitate this part of the mechanism. However, in the single crystals, the hydrogen atoms diffuse so deep that they are no longer accessible to the adsorbed alkenes. In contrast, in case of the nanoparticles, the hydrogen is readily available to the adsorbed alkene and hydrogenation is favored. Nanoparticles may contain a few tens to several thousand metal atoms, with their sizes varying from 1 to 50 nm, with properties depending on the size

Metal nanoparticles can either be monometallic, bimetallic or multimetallic. The most studied nanoparticle catalysts are the noble metals including Ru, Rh, Pd, Pt, and Au. However because of costs, transition metal nanoparticles (Co, Ni, and Fe) are now being investigated since they mimic metal surface activation and catalysis and exhibit selectivity. Bimetallic and multimetallic nanoparticles, the addition of additional metal(s) allows control of activity, selectivity, and stability of the catalyst in certain reactions since they provide more tunable variables.

Most commercial catalysts are manufactured by impregnating with the active agents only and external thin layer of alumina pellets. The alumina used as Pd catalyst support in this reaction contains mostly the alpha phase alumina since it possesses relatively low specific surface area and low acidity compared to other transition aluminas (Wongwaranon *et al.*, 2008). Palladium is known to be quite effective for selective hydrogenation due to the reactions of olefins are inhibited by the stronger adsorption of acetylenics compounds and 1,3-butadiene (Hub *et al.*,

1988). The overall Pd content ranges typically within 0.1-0.5% (w/w). The impregnation of noble metals on metal oxides is a common synthesis pathway for hydrogenation-reaction catalysts. The rate of hydrogenation can depend on numerous parameters, such as loading and size of the noble metal particles involve in promoted metal, the distribution or concentration profile of the active component throughout a catalyst particle, and the feature of support material (Cukic *et al.*, 2007).

Boudjahem *et al.* (2007) studied the benzene hydrogenation over Ni–Cu/SiO₂ catalysts prepared by aqueous hydrazine reduction. They found that the presence of copper decreased the nickel phase dispersion as well as the conversion whereas it increased the carbon deposit in benzene hydrogenation. The decrease of the metal surface and catalytic properties was ascribed to both changes in the nickel morphology and Ni–Cu interactions

Han *et al.* (2007) studied the hydrogenation of *p*-chloronitrobenzene over carbon nanotubes supported platinum catalysts modified by Mn, Fe, Co, Ni and Cu. Their results showed that both catalytic activities and yields of *p*-CAN were all improved with the additions of small amount of transition metal to Pt/CNTs catalyst except Cu. The effect of transition metal may be interpreted by electronic effect. PtFe/CNTs catalyst exhibited the best catalytic activity, and PtMn/CNTs catalyst exhibited the highest yield of *p*-CAN (98.5 mol%). Pt/CNTs catalyst reduced by KBH₄ exhibited good catalytic activity and stability on the hydrogenation of *p*-CNB. Higher yields of *p*-CAN and lower catalytic activities were obtained for PtM/CNTs(II) catalysts. PtNi/CNTs(II) catalyst exhibited the highest yield of *p*-CAN (97.8 mol%)

Ruijun *et al.* (2007) studied selective hydrogenation of 1,3-butadiene on Pd-Ni bimetallic catalyst. Their results showed that the Pd-Ni bimetallic structure exhibited higher hydrogenation activity than its monometallic counterparts. The activity of the catalysts followed the trend of Pd-Ni > Pd > Ni. The selectivity was evaluated with supported catalysts in both batch and flow reactors. The Pd-Ni, Pd and Ni catalysts supported on γ -Al₂O₃ showed similar total selectivity to butenes, while Pd-Ni/ γ -Al₂O₃ exhibited the highest 1-butene selectivity at similar conversions. The high hydrogenation activity and 1-butene selectivity made Pd-Ni/ γ -Al₂O₃ a better catalyst for 1,3-butadiene removal than the Pd monometallic catalyst.

2.4.1 Catalysts Hydrogenation of Acetylene

The selective hydrogenation of acetylene in ethylene rich stream is crucial process since acetylene poisons the polymerization catalysts. Pd-based catalyst supported on alumina with low Pd loading is typically employed for this reaction due to its good activity and selectivity and the easily desorption of ethylene on the catalyst surface. With respect to selectivity changes, catalysts of low Pd dispersion have been suggested to give better selectivity towards ethylene at high acetylene conversions

Wongwaranon *et al.* (2008) studied the Pd catalysts supported on nanocrystalline α -Al₂O₃ and Ni-modified α -Al₂O₃ in selective hydrogenation of acetylene. Nanocrystalline α -Al₂O₃ and Ni-modified α -Al₂O₃ have been prepared by sol-gel and solvothermal methods and employed as supports for Pd catalysts. Catalytic performances in selective hydrogenation of acetylene were found to be superior those of the commercial α -Al₂O₃ supported one. Ethylene selectivities were improved in the order: Pd/Ni-modified α -Al₂O₃-sol-gel > Pd/Ni-modified α -Al₂O₃-solvothermal \approx Pd/ α -Al₂O₃-sol-gel > Pd/ α -Al₂O₃-solvothermal \gg Pd/ α -Al₂O₃ commercial.

Sangkhum *et al.* (2009) used nanocrystalline Fe-modified α -Al₂O₃ prepared as supports for Pd catalysts resulted in an improved catalyst performance in selective acetylene hydrogenation. Moreover, the amount of coke deposits was reduced due to lower acidity of the Fe-modified α -Al₂O₃ supports.

Lee *et al.* (2011) used Ni-added Pd-Ag catalysts showed higher conversions than Ni-free Pd-Ag catalyst in the selective hydrogenation of acetylene. Ethylene selectivity increased by Ni addition because the amounts of surface hydrogen originating from the Pd bulk phase, which was responsible for the full hydrogenation of ethylene to ethane, were decreased due to the presence of Ni at the sub-surface of Pd-Ag particles. Added Ni also modified the geometric nature of the Pd surface by blocking large ensembles of Pd into isolated ones, which eventually improved ethylene selectivity.

Insorn *et al.* (2015) studied selective hydrogenation of mixed C4 containing high vinyl acetylene by Mn-Pd, Ni-Pd and Ag-Pd on Al₂O₃ catalysts reported that Mn-promoted Pd/Al₂O₃ catalyst at a 2:1 Pd/Mn molar ratio significantly increases the activity and moderately increases the yield and selectivity for 1,3-butadiene. Adding Ni to Pd/Al₂O₃ catalysts improves only the activity but adding Ag even inhibits the activity.

Huang *et al.* (2007) studied selective hydrogenation of acetylene in the presence of ethylene by using Pd, Ni, Ag, Pd-Ni and Pd-Ag supported on Al₂O₃ and β -zeolite as a catalyst. From the results, they found that Pd-Ag/Al₂O₃ catalysts have not only higher selectivity for acetylene hydrogenation in the presence of ethylene than either Pd or Ag monometallic catalyst but also it higher selectivity than Pd-Ni catalysts. For alloying Pd catalyst with Ni, they found that the selectivity of acetylene hydrogenation of Pd-Ni/Al₂O₃ catalysts and Pd/Al₂O₃ were similar but the selectivity of acetylene hydrogenation of Pd-Ni/Na⁻ β -zeolite higher than Pd/Na⁻ β -zeolite and they concluded that the Na⁻ β -zeolite-supported catalysts exhibited higher selectivity than their γ -Al₂O₃ counterparts, the Pd/Na⁻ β -zeolite, Pd-Ni/Na⁻ β -zeolite showed higher hydrogenation activities than those on the Pd/Al₂O₃, Pd-Ni/Al₂O₃. Although hydrogenation activity of Pd-Ag/Na⁺ β -zeolite is lower than Pd-Ag/Al₂O₃.

2.4.2 Catalysts Hydrogenation of Hexyne

Partial hydrogenation of alkynes has industrial and academic on a large scale, especially those with high selectivity. The development of bimetallic systems has been investigated.

Maccarrone *et al.* (2012) studied hydrogenation of 3-hexyne using low-loaded palladium mono and bimetallic supported on alumina. XPS results indicated the presence of electron rich and electron deficient palladium species on the surface of bimetallic systems which showed higher activities and very similar selectivities than the monometallic system and further than the Lindlar catalyst.

Anderson *et al.* (2009) prepared the Pd/Al₂O₃ catalyst of different loading Bi and Pb in hydrogenation of 1-hexyne and 2-hexyne. Their results showed that while Bi had little effect on the rate of the 1-hexyne hydrogenation, rate of

subsequent reaction of the 1-hexyne formed were suppressed. Bi was a more effective modifier than Pd, situation was reversed when reactions were performed using 2-hexyne. Results are discussed by the reaction mechanism and key intermediates in the process and roles of bismuth, relative to lead, in creating an appropriate ensemble of surface Pd atoms to permit control of selectivity.

Ando *et al.* (2001) studied the liquid phase selective hydrogenation of (E)-2-hexenal to (E)-2-hexen-1-ol over Co-based bimetallic catalysts. The catalysts they used were (M-Co)/Al₂O₃, M= Pd, Pt, Ru, Rh, Sn, Fe, Cu). They found that the hydrogenation of (E)-2-hexenal gave (E)-2-hexen-1-ol (unsaturated alcohol, UOL), hexanal (saturated aldehyde, SAL) and 1-hexanol (saturated alcohol, SOL) by using the M-Co/Al₂O₃ bimetallic catalysts. Besides the hydrogenated products, 1-1-diethoxy-2-hexene (Acetal) was formed in a small quantity. From this result, they conclude that Pd-Co/Al₂O₃ showed the highest activity among the catalysts tested.