CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Mixed C4 Hydrocarbons

Mixed C4 hydrocarbons are a mixture of hydrocarbons which have 4 carbon atoms in its molecule. They compose of butadienes, butenes, butanes, isobutylene and C4-acetylene. Generally, mixed C4 hydrocarbons are a product from fluid catalytic cracking unit. The typical composition of mixed C4 stream which is originated in fluid catalytic cracking unit is shown in Table 2.1.

Table 2.1 Typical composition of mixed C4 stream from fluid catalytic cracking unit

Compound	wt%
1,3-Butadiene	35-50
1,2-Butadiene	0-0.5
Isobutylene	20-25
Butene	20-25
Butane	5-10
Propane/Propylene	0-1
C4-acetylene	0.5-1.5

In mixed C4 stream, there are some components which have high value since it can be used as a feedstock in many downstream processes. For example 1,3-butadiene is used as a precursor for polybutadiene and styrene-butadiene rubber production, 1-butene is used as a co-monomer with ethylene in order to make linear low density polyethylene (LLDPE), isobutylene is used as a feedstock for producing methyl *tert*-butyl ether (MTBE) or ethyl *tert*-butyl ether (ETBE) and butane can be used as the liquefied petroleum gas (LPG). Therefore, each high value hydrocarbon will be separated from mixed C4 stream before using as a feedstock in downstream processes. Other C4-hydrocarbons which have lower value like C4-acetylene, 2-butene and 1,2-butadiene are removed or converted to higher value hydrocarbon.

In the typical C4 separation and purification plant, the mixed C4 hydrocarbon from the fluid catalytic cracking unit is fed to the butadiene extraction process in order to extract and purify 1,3-butadiene from the mixed C4 first. Moreover, C4-acetylene are separated from the mixed-C4 stream in this process for the safety reason because it is very reactive to form peroxide and can lead to self-explosion. The raffinate stream from the butadiene extraction process mainly composes of butenes and butane but it still has small amount of 1,3-butadiene which have to be eliminated before sending to downstream process. The elimination of 1,3-butadiene from raffinate stream often use hydrogenation process. Moreover, the hydrogenation process can be also used to upgrade low value hydrocarbon like C4-acetylene to higher value hydrocarbon such as 1,3-butadiene or 1-butene. The outlet stream from hydrogenation process is called Raffinate-1. Raffinate-1 is fed to etherification process in order to convert isobutene to other compound such as methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE). Then the outlet stream which is called Raffinate-2 is fed to 1-butene process in order to separate 1-butene from Raffinate-2. Then, the raffinate stream from this process is used as liquefied petroleum gas (LPG).

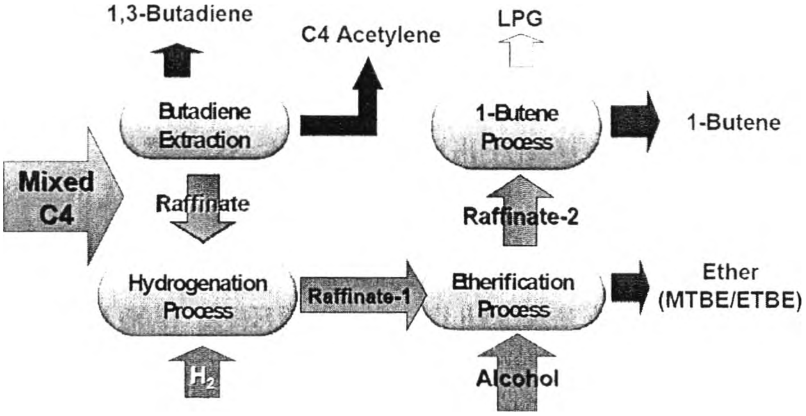

Figure 2.1 The diagram of the typical C4 separation and purification plant.

From the typical C4 separation and purification plant, C4-acetylene is separated from mixed C4 stream and burnt away. However C4-acetylene can be upgraded to higher value hydrocarbon by using the selective hydrogenation process. The problem of this process are a low 1,3-butadiene selectivity and stability of commercial Pd catalyst when using highly concentrated vinylacetylene stream.

2.2 Hydrogenation

A hydrogenation is a chemical reaction which is an addition of pair of hydrogen atoms to an unsaturated molecule. The hydrogenation is widely used in the synthesis and manufacture of fine and industrial chemicals.

$$\mathrm{R{=}R} + H_2 \longrightarrow \mathrm{R{-}R}$$

$$\mathrm{R{\equiv}R} + H_2 \longrightarrow \mathrm{R{=}R}$$

Figure 2.2 Hydrogenation reaction of unsaturated hydrocarbon.

2.2.1 Hydrogenation of C4 Hydrocarbons

C4 hydrocarbons compose of many unsaturated hydrocarbons such as C4-acetylenic compound, butadienes and butenes. So the hydrogenation reaction of C4 hydrocarbons is complicated. However many researchers have tried to study the kinetics and mechanisms of hydrogenation reaction of C4 hydrocarbons.

Ryndin *et al.* (1988) studied the gas-phase hydrogenation of vinylacetylene by using Pd/SiO_3 and Pd/γ-Al_2O_3 as the catalysts. The result from reaction study was shown in Figure 2.3. They suggested that vinylacetylene would be hydrogenated to form butadiene and butenes (a mixture of butene-1, *cis*- and *tran*-butene-2). Then butadiene could be further hydrogenated to butenes and butenes could be hydrogenated to butane. The possible reaction was shown in Figure 2.4. where VA =Vinylacetylene, DV =1,3-Butadiene, $B^{=}$=1-Butene, *cis*-2-Butene, *trans*-2-Butene, B =Butane.

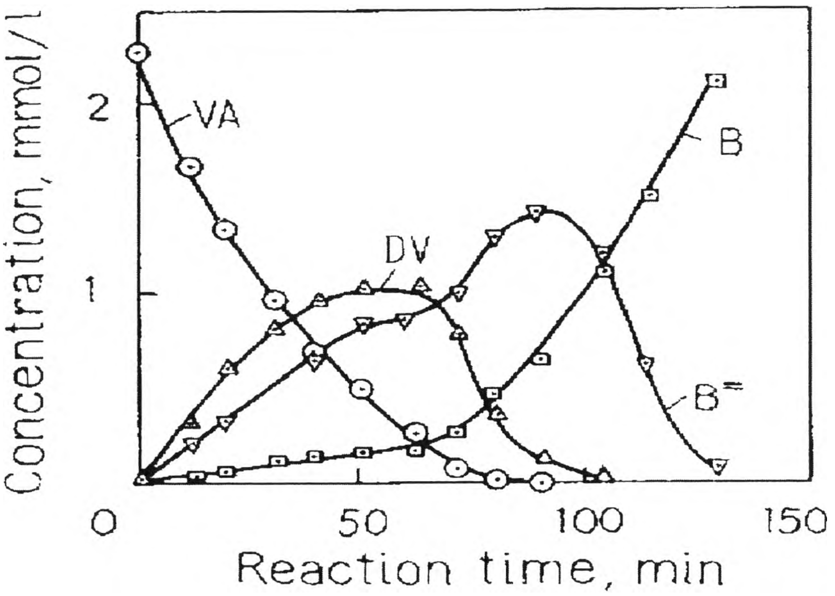

Figure 2.3 The plot of reaction mixture composition versus reaction time for 1.9% Pd/Al_2O_3 catalyst in gas-phase hydrogenation of vinylacetylene (Ryndin *et al.*, 1988).

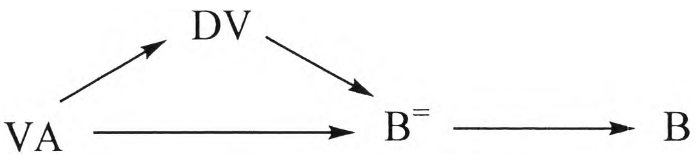

Figure 2.4 The possible reaction of vinylacetylene hydrogenation (Ryndin *et al.*, 1988).

Ardiaca *et al.* (2001) investigated the kinetics of liquid-phase hydrogenation of 1,3-butadiene and *n*-butene on commercial Pd catalysts by using three reactor types including a slurry reactor, a rotating-basket reactor and a recirculation system with an external fixed-bed reactor. They suggested that the reaction network of hydrogenation of butadiene could be sketched as in Figure 2.5, where BD ≡ 1,3-Butadiene, 1-BE ≡ 1-Butene, cBE ≡ *cis*-2-Butene, tBE ≡ *trans*-2-Butene and BA ≡ *n*-Butane. From the reaction network of hydrogenation of butadiene, butadiene could be hydrogenated to three isomers of butene first and then each of these butenes could be isomerized and could be further hydrogenated to butane.

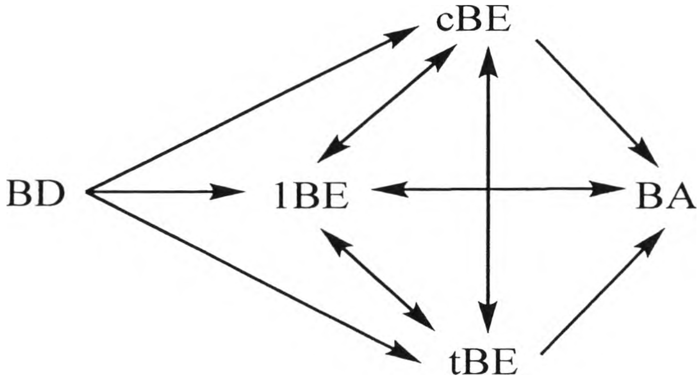

Figure 2.5 Overall reaction network of hydrogenation reaction of 1,3-butadiene (Ardiaca *et al.*, 2001).

They confirmed this reaction network model of hydrogenation reaction by comparing with the experimental data. They found that the experimental result was consistent with the predicted reaction network.

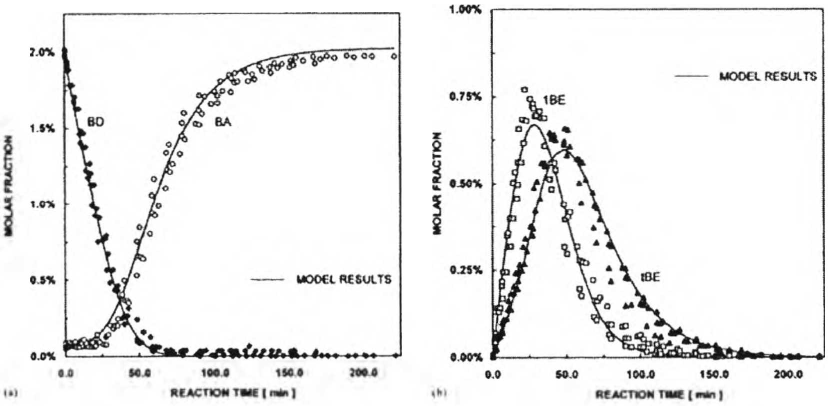

Figure 2.6 Comparison between predicted composition and experimental results of hydrogenated products as a function of time (Ardiaca *et al.*, 2001).

Moreover, they also found that the slurry reactor had many limitations in using a catalyst with small particle. Therefore, the slurry reactor was not considered. The rotating basket reactor had lower performance than the external fixed bed reactor as shown in the Figure 2.7. They concluded that the external fixed bed reactor was the best reactor of 3 type of reactor which they studied.

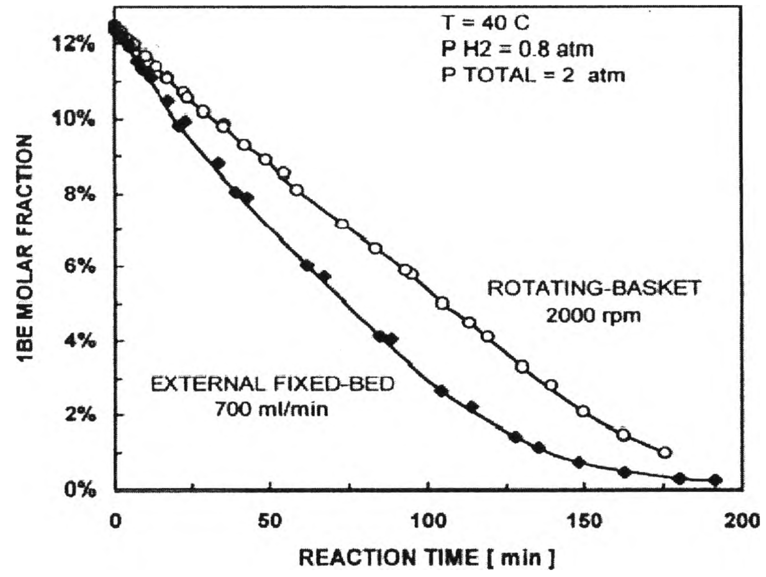

Figure 2.7 The consumption of 1-butene: comparison between the rotating-basket reactor and recirculation system with an external fixed-bed reactor (Ardiaca *et al.*, 2001).

Grant *et al.* (1976) studied 1,2-Butadiene hydrogenation over Ni powder, Ni/Al_2O_3 and Ni/SiO_2. They found that almost of 1,2-butadiene were hydrogenated to 1-butene, *cis*-2-butene and *trans*-2-butene. Moreover, 1,2-butadiene could be slowly isomerized to 1,3-butadiene.

Seth *et al.* (2007) studied the liquid-phase selective hydrogenation of 1,3-butadiene in mixture with isobutene on a Pd/α-alumina catalyst in a semi-batch reactor. They did the experiment by using four types of starting reactants which were 1-butene, isobutene, 1,3-butadiene and 5 wt% of 1,3-butadiene in a mixture with isobutene. They found that when 1-butene was used as the starting reactant, *cis*- and *trans*-2-butene and *n*-butene were the only products of hydrogenation. When isobutene was used as a starting reactant, isobutane was the only product. When the mixture of 1,3-butadiene and isobutene was used as a starting reactant, isobutane, 1-butene, 2-butenes and butane were produced. From this results, they concluded that isobutane was the only product for the hydrogenation of isobutene, so the reaction of hydrogenation of isobutene could be separated from reaction network of hydrogenation of 1,3-butadiene and they proposed the reaction network of hydrogenation of 1,3-butadiene and isobutene as shown in Figure 2.8.

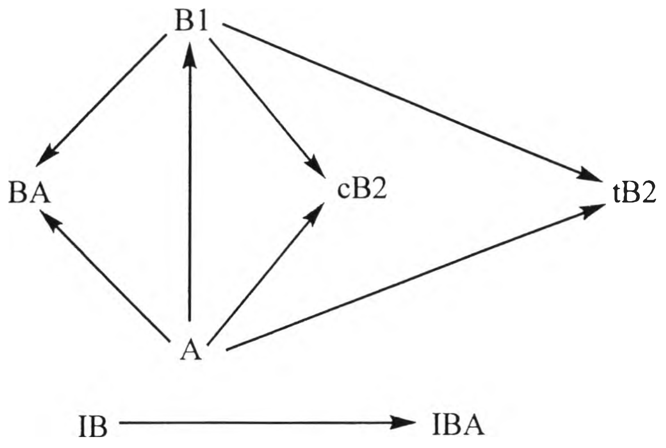

Figure 2.8 The reaction network of hydrogenation of 1,3-butadiene and isobutene, A≡ 1,3-Butadiene, B1≡ 1-Butene, cB2≡ *cis*-2-Butene, tB2≡ *trans*-2-Butene, BA≡ *n*-Butane, IB≡ Isobutene, IBA≡ Isobutane (Seth *et al.*, 2007).

Alves *et al.* (2007) studied the liquid-phase hydrogenation of 1-butyne over Pd/Al_2O_3 catalyst by using recirculation system with an external fixed-bed reactor. They found that 1-butyne was only hydrogenated to 1-butene until 1-butyne reached high conversion and then 1-butene reacted to form butane, *cis*- and *trans*-2-butene as shown in Figure 2.9.

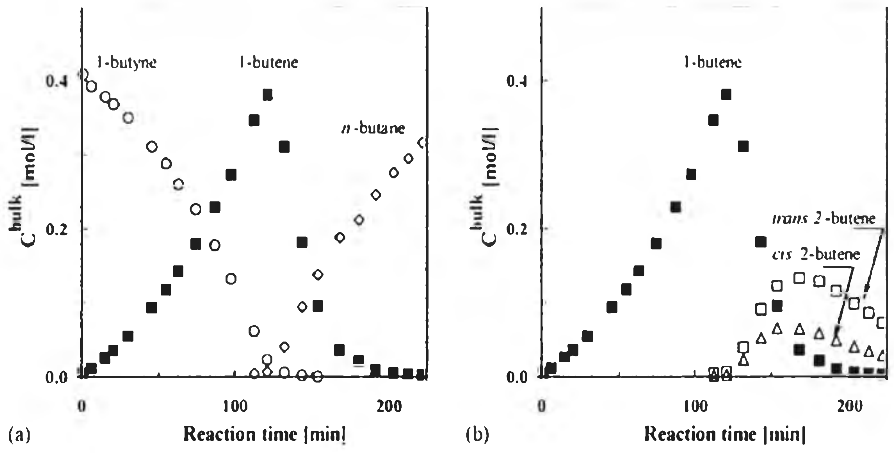

Figure 2.9 Variation of hydrocarbon bulk concentrations with reaction time (Alves *et al.*, 2007).

From previous study of hydrogenation of C4-hydrocarbon, the hydrogenation reaction network of C4-hydrocarbon can be written as shown in Figure 2.10.

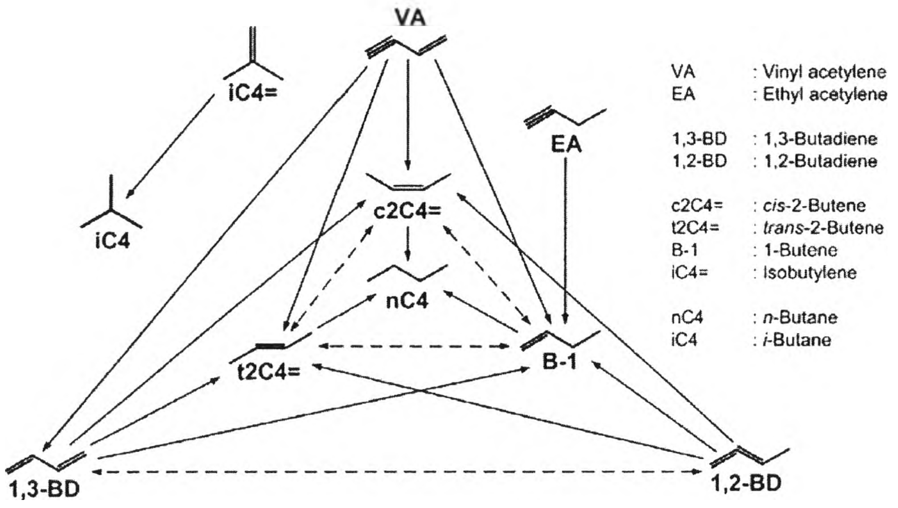

Figure 2.10 The possible reaction of hydrogenation of C4-hydrocarbon.

2.2.2 Catalyst for Selective Hydrogenation of Acetylenic Compound and Butadiene

The catalyst for selective hydrogenation of unsaturated hydrocarbons such as acetylene and butadiene has been widely studied, especially the Pd-based catalysts. An addition of second metal atom to Pd catalyst on various supports is a topic which many researchers have been interested in.

Desiderio *et al.* (1975) claimed a patent about selective hydrogenation of vinylacetylene. They studied the hydrogenation of the mixture of 0.7-1.0% vinylacetylene in butadiene by using 2 packed-bed reactors which were packed by 0.05-0.2% Pd on alumina in the mixed phase condition (pressure 6-8 atm and temperature 40-60 ^{o}C) and the liquid phase condition (pressure 20 atm). They found that the vinylacetylene hydrogenation in the mixed phase condition showed greater vinylacetylene conversion and 1,3-butadiene selectivity than vinylacetylene hydrogenation in the liquid phase condition.

Pattamakornsan *et al.* (2010) studied the effect of mixed Al_2O_3 structure between θ- and α-Al_2O_3 on the properties of Pd/Al_2O_3 in the gas-phase selective hydrogenation of 1,3-butadiene under industrial simulated conditions. The catalysts which they used were 0.2% Pd on 100/0, 80/20, 40/60 and 0/100 (%) θ/α-Al_2O_3. The reaction study was performed at 50 ^{o}C and atmospheric pressure. They found that the BET surface area, pore volume and acidity of Al_2O_3 supports decreased dramatically as wt% of α-Al_2O_3 increased and the number of Pd active site also decreased as the wt% of α-Al_2O_3 increased which corresponded to the decrease of Pd dispersion and increase of Pd^0 particle size. From the reaction study, they found that Pd supported on 80% θ- and 20% α-Al_2O_3 showed the best performance because it exhibited both low loss of 1-butene product and low butane selectivity.

Wongwaranon *et al.* (2008) studied the selective hydrogenation of acetylene by using Pd catalysts supported on nanocrystalline α-Al_2O_3 and Ni-modified α-Al_2O_3 which were prepared by sol-gel and solvothermal methods. They found that the addition of Ni resulted in decrease of acid sites on the alumina support and the amounts of CO chemisorption decreased which corresponded to the decreasing in Pd metal dispersion with decreasing amounts of added Ni atoms. From the reaction test, they found that both Pd catalysts supported on nanocrystalline α-

Al_2O_3 and Ni-modified α-Al_2O_3 showed higher catalytic performances in acetylene hydrogenation than commercial α-Al_2O_3 and Pd/Ni-modified α-Al_2O_3 exhibited higher selectivity than Pd/α-Al_2O_3.

Tew *et al.* (2011) investigated the formation and characterization of PdZn alloy of pentyne hydrogenation catalyst. Prepared catalysts which were reduced at 150, 200, 300 and 400 °C would be used to characterize by XRD, XAS and STEM and perform the reaction testing in the fixed-bed reactor. They found that PdZn alloy would be formed by reducing Pd/ZnO catalyst at higher than 100°C and the amount of alloy would be increased with increasing reduction temperature. The PdZn alloy would change the electronic property of Pd and dilute the Pd site at surface which caused to increase the selectivity of pentene and decrease pentane formation.

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 Al_2O_3 and β-zeolite as a catalyst. For the effect of bimetallic formation, they found that Pd-Ag bimetallic catalysts showed higher ethylene selectivity for acetylene hydrogenation than either Pd or Ag monometallic catalyst and it showed higher ethylene selectivity than Pd and Pd-Ni catalysts. For alloying Pd catalyst with Ni, they found that the selectivity of acetylene hydrogenation of Pd-Ni/Al_2O_3 catalysts and Pd/Al_2O_3 were similar but the selectivity of acetylene hydrogenation of Pd-Ni/Na^+- β-zeolite was higher than Pd/Na^+- β-zeolite. For the effect of catalyst support, they found that The Na^+-β-zeolite-supported catalysts exhibited higher ethylene selectivity than their γ-Al_2O_3 and Na^+- β-zeolite-supported Pd and Pd-Ni catalysts showed higher hydrogenation activities than those on the γ- Al_2O_3-supported but hydrogenation activity of Pd-Ag/ β-zeolite was lower than Pd-Ag/ γ- Al_2O_3.

Pachulski *et al.* (2011) compared the performance and regeneration of Pd-Ag bimetallic catalysts for the selective hydrogenation of acetylene with both Pd and Ag monometallic catalysts. They found that Pd-Ag/Al_2O_3 catalysts were more stable than the Pd/Al_2O_3 catalyst and the Pd-Ag/Al_2O_3 catalyst which contained Ag/Pd-ratio in the bulk of 0.41 has the highest long-term stability. This low silver amount caused a higher dilution of the Pd surface area than the higher Ag amount within the investigated catalyst. Moreover they also found the used catalysts could be clean completely from the hydrocarbon depositions by using both thermal treatment in air and treatment in hydrogen at temperature greater than 120 °C.

Sarkany *et al.* (2002) studied the hydrogenation of acetylene in an atmospheric pulse-flow reactor by using low loaded Pd and Pd-Au/SiO_2 as catalysts. The catalysts which they used were 0.2 wt% Pd/SiO_2, 2 wt% Pd/SiO_2, 0.2 wt% Pd-0.33 wt% Au/SiO_2 and 2 wt% Pd-0.35 wt% Au/SiO_2. They found that Pd/SiO_2 exhibited both higher over-hydrogenation and higher C4 formation than Pd-Ag/SiO_2 which had the same amount of loaded Pd. So they concluded that addition of Au to Pd/SiO_2 would decrease the carbon coverage and improve the ethane selectivity.

Pattamakomsan *et al.* (2010) studied the hydrogenation of 1,3-butadiene over Pd and Pd-Sn catalysts supported on mixed phase □/α- and pure α-alumina. The catalysts which they studied were 0.5 wt% Pd/α-Al_2O_3, 0.5 wt% Pd/mixed Al_2O_3, 0.5 wt% Pd-0.2 wt% Sn/α-Al_2O_3, 0.5 wt% Pd-0.2 wt% Sn/mixed Al_2O_3. The reaction study was carried out in fixed-bed reactor at 30-70 °C and atmospheric pressure. They found that addition of Sn would modify the electronic properties and dilute the Pd surface atoms. It caused to decrease butane formation and hinder isomerization of 1-butene. Pd and Pd-Sn supported on mixed phase alumina were higher dispersion than Pd and Pd-Sn supported on α-phase alumina. The Pd-Sn supported on mixed phase alumina catalyst was the best catalyst which showed both good selectivity and activity.

Furlong *et al.* (1994) studied the selective hydrogenation of 1,3-butadiene in 1-butene over alumina supported Pd and Pd/Cu catalyst in both batch and plug flow reactor. They found that the Pd-Cu/Al_2O_3 catalyst was more selective and active than Pd/Al_2O_3 catalyst and all 1,3-butadiene would be hydrogenated without butane production when use Pd-Cu/Al_2O_3 as a catalyst.

Lederhos *et al.* (2011) studied the partial hydrogenation of hept-1-yne by using supported Pd and W as the catalysts. The prepared catalysts were Pd and W monometallic catalysts and Pd-W and W-Pd bimetallic catalysts. The reaction was carried out in stirred tank batch reactor at 303 K and 150 kPa. They found that the W monometallic catalyst had low heptene selectivity for partial hydrogenation of hept-1-yne and the addition of Pd to W monometallic catalysts (W-Pd bimetallic catalysts) greatly improved the selectivity to the desired product. The Pd monometallic catalyst exhibited high heptene selectivity and low total conversion. The addition of W to Pd monometallic catalyst (Pd-W bimetallic catalyst) would increase total conversion 3.5 times. They concluded that the addition of a second metal to Pd and W monometallic catalysts would greatly improve both activity and conversion of hept-1-yne.

Kim *et al.* (2011) studied performance of Cu- and Ag-promoted Pd catalysts in acetylene hydrogenation. They found that both of Ag- and Cu-promoted Pd/Al_2O_3 catalysts gave the higher ethylene selectivity than Pd/Al_2O_3 catalyst. This improvement could be described by changing of electronic and geometric properties of Pd catalysts when adding Cu and Ag atoms.

2.3 Deactivation of Pd Based Catalyst

The deactivation of catalyst can occur from many causes for example poisoning, formation of deposits, thermal degradation, mechanical deactivation and leaching. For Pd catalyst which is used in the liquid phase hydrogenation of highly concentrated vinylacetylene mixed C4, the deactivation mainly occur from coking, poisoning and Pd leaching.

The coking is the deactivation of catalyst which occurs from blocking pore and covering active site of the catalyst by carbonaceous compounds which are formed by side reactions. In case of hydrogenation of 1,3-butadiene over Pd/Al_2O_3, the oligomer and polymer are found on the spent catalyst. They create diffusion problem by decreasing the effective diffusion coefficient and lead to decreasing in selectivity and increasing in 1-butene isomerization and hydrogenation rates.

The poisoning is the loss of activity due to the strong chemisorption on the active sites of impurities in the feed stream. The poison block the active site (geometric effect) or change the adsorptivity of other species by the electronic effect or change the chemical nature of the active site. The poisons of Pd catalyst are CO, S, Pb, CS_2, thiophene, NO, N_2O and H_2S.

Leaching is the loss of precious metal because of the formation of soluble complex compounds. The nitro compounds are well known agents to mobilize Pd because it can oxidize the Pd metal easily and then lost in the bulk liquid. Moreover, the product contamination is another effect from leaching. For preventing Pd-leaching, the hydrogen should be fed in the liquid reaction medium in order to keep the Pd in a well-reduced.