CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Mixed C4 hydrocarbons

In petrochemical industry, Fluid Catalytic Cracking Unit (FCC) is utilized to produce several products including C2 or C3 olefins, hydrogen, methane or even mixed C4 hydrocarbons. Mixed C4 hydrocarbons are a mixture of hydrocarbons. Its molecule composes of four carbon atoms. Typically, the composition of mixed C4 from FCC unit is shown in Table 2.1.

Table 2.1: Typical composition of mixed C4 stream from fluid catalytic cracking unit (FCC), (Bangkok Synthetics Co., Ltd)

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

Several compounds in mixed C4 stream are economic value which can be utilized as starting materials in many downstream processes such as 1,3-butadiene is used as a precursor for polybutadiene and styrene-butadiene rubber production, isobutylene can be used as a feedstock for producing methyl *tert*-butyl ether (MTBE) or ethyl *tert*-butyl ether (ETBE), 1-butene is used as a co-monomer with ethylene to produce linear low density polyethylene (LLDPE) and butane is also a component in liquefied petroleum gas (LPG). Conversely, other compounds in mixed C4 which have low value such as C4-acetylene, 2-butene and 1,2-butadiene, several industrial plants will remove or convert to higher value products.

2.2 Hydrogenation of 1-hexyne

In this study, 1-hexyne is selected to be used as a model acetylene compound for liquid phase hydrogenation. The desired product of 1-hexyne selective hydrogenation is 1-hexene which can be homo- or co-polymerized with ethylene to produce linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE). Most polyethylene (PE) products are used for packaging (film, bags, sealings, bottles/drums etc), due to its low cost price. Other important markets are piping and tubing, due to good chemical resistance and strength of PE.

2.2.1 Catalysts for 1-hexyne hydrogenation

In general, palladium monometallic catalyst gives a high catalytic performance in the partial hydrogenation reactions of alkynes and dienes to olefins. In the same way, using bimetallic catalyst is an efficient way to improve the catalytic performances of catalysts. Kim *et al.* (2011) studied the performance of Cu-and Ag-Promoted Pd catalysts in acetylene hydrogenation. The prepared catalysts were Pd, Pd-Cu and Pd-Ag supported on alumina catalysts. From the results, they reported that both of the Cu- and Ag-promoted Pd catalysts showed the higher ethylene selectivity than Pd catalyst. Moreover, ethylene selectivity increased with increasing the amount of promoter. For catalytic activity, Cu-promoted catalyst was more activity than Ag-promoted catalyst and Lederhos *et al.* (2011) also reported that the addition of a second metal to Pd and W monometallic catalysts to form Pd-W and W-Pd bimetallic catalysts would greatly improve both selectivity and conversion of hept-1-yne.

From these researches, Pd-Cu and Pd-W catalysts show higher selectivity than Pd catalyst in acetylene hydrogenation and 1-heptyne hydrogenation respectively. Therefore, the authors believe that 1-hexene selectivity can be improved by Pd-Cu and Pd-W catalysts when using in hydrogenation of 1-hexyne.

2.3 Hydrogenation reaction

Hydrogenation is a chemical reaction, typically constitutes the addition of pairs of hydrogen atoms to a molecule, generally an alkene. The process is commonly employed to reduce or saturate organic compounds. Catalysts are required for the reaction to be usable; non-catalytic hydrogenation takes place only at very high temperatures. Hydrogen adds to double and triple bonds in hydrocarbons. Hydrogenation of unsaturated hydrocarbons has been utilized in many applications such as widely used in the synthesis and manufacture of fine and industrial chemicals or even used to treat or purify the feeds or raw materials. The hydrogenation reaction of unsaturated hydrocarbon has shown in Fig 2.1.

$$R = R \quad + \quad H_2 \longrightarrow \quad R - R$$

$$R \equiv R \quad + \quad H_2 \longrightarrow \quad R = R$$
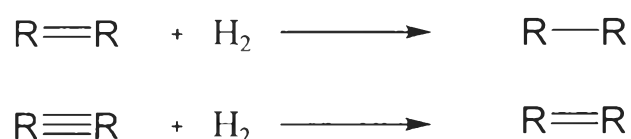
Figure 2.1: Hydrogenation reaction of unsaturated hydrocarbon.

2.3.1 Hydrogenation reaction mechanism of C4-C6 hydrocarbons

Owing to the mixed C4 hydrocarbons have several unsaturated hydrocarbon compounds which compose of butadiene, butene, butane, isobutylene and C4-acetylene and hydrogenation of 1-hexyne also gives several compounds such as 1-hexene, cis-2-hexene, trans-2-hexene and n-hexane. Accordingly, the mixed C4 and 1-hexyne hydrogenation reaction will be very complex reaction. From this reason challenge many researchers have tried to study the kinetics and mechanisms of hydrogenation reaction of C4-C6 hydrocarbons.

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. The starting reactants were 1-butene, isobutene or a 5 wt% mixture of butadiene in isobutene. From the experiment when they used 1-butene as the starting reactant, cis- and trans-2-butene and n-butane were the only products of hydrogenation. When they used isobutene as the starting reactant, isobutane was the only product. The hydrogenation of mixture of butadiene and isobutene produced

isobutane, 1-butene, *cis*- and *trans*-2-butene and *n*-butane. From this results, they summarized that isobutane is the only product of the isobutene selective hydrogenation so they suggested that the reaction of hydrogenation of isobutene should be separated from reaction network of hydrogenation of 1,3-butadiene and the reaction network of hydrogenation of butadiene and isobutene as shown in Figure 2.2
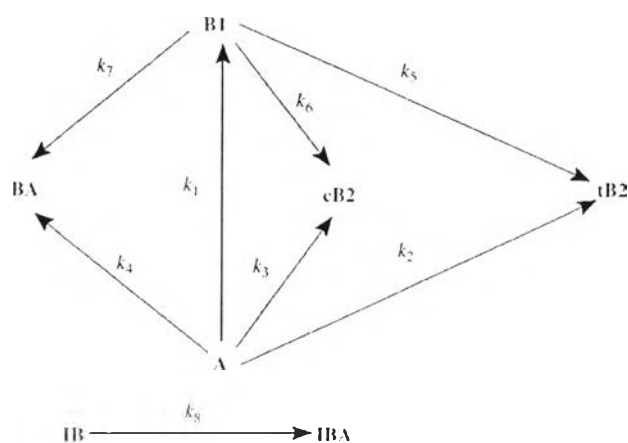
Figure 2.2: The reaction network, A = 1,3-butadiene, B1 = 1-butene, cB2 = *cis*-2-butene, tB2 = *trans*-2-butene, BA= n-butane, IB = isobutene, IBA = isobutane. (Seth *et al.*, 2007)

Alves *et al.* (2007) studied the liquid-phase hydrogenation of 1-butyne over a commercial Pd/Al_2O_3 catalyst. The reaction study was carried out in recirculation system with an external fixed-bed reactor. From the results, they found that 1-butyne was only product yield of the 1-butyne hydrogenation until 1-butyne reaches a high level of conversion after that 1-butene neatly reacts to form n-butane and *cis*-, *tran*-2 butene.
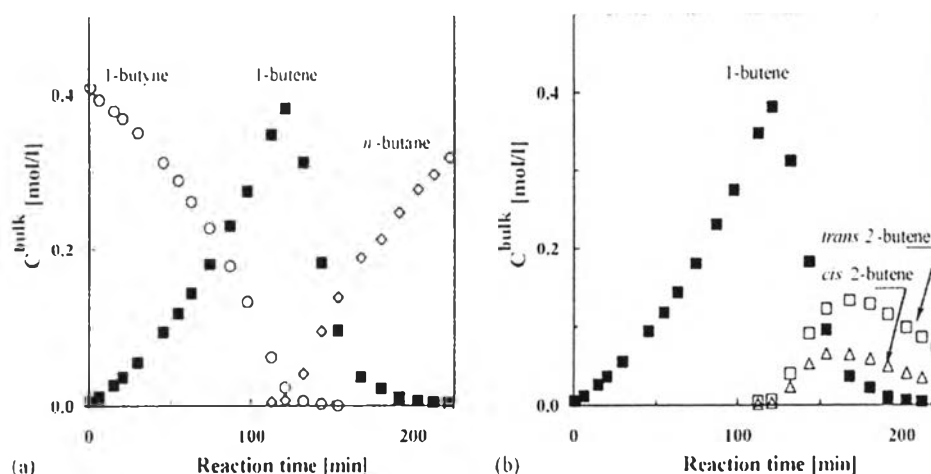
Figure 2.3: Variation of hydrocarbon bulk concentrations with reaction time.

(Alves *et al.*, 2007)

From previous study of hydrogenation of C4-hydrocarbon, it can be concluded that the hydrogenation reaction network of C4-hydrocarbon could be written as shown in Figure 2.4.
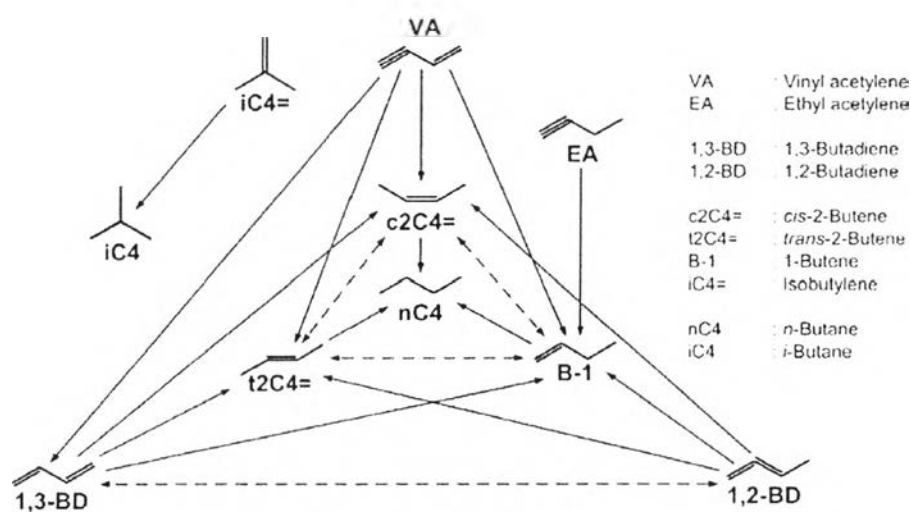
Figure 2.4: Overall reaction network of hydrogenation of C4-hydrocarbon.

Grant *et al.* (1976) studied 1,2-butadiene hydrogenation over Ni powder, Ni/SiO$_2$ (type A) and Ni/Al$_2$O$_3$ (type B). From the results, they found that almost 1,2-butadiene would be hydrogenated to form 1-butene, *cis*-2-butene and *trans*-2-butene. And others could be slowly isomerized to form 1,3-butadiene.

Ryndin *et al.* (1988) studied the gas-phase hydrogenation of vinyl acetylene. The catalysts were Pd/SiO_3 and $Pd/\gamma-Al_2O_3$. From the reaction study in Fig 2.5, they found that the hydrogenation of vinyl acetylene would form butenes (a mixture of butane-1, *cis*-butene-2 and *trans*-butene-2) and 1,3-butadiene. And the 1,3-butadiene could be further hydrogenated to form butenes and butenes could be hydrogenated to form butane. Where the (VA) = vinyl acetylene, (DV) = 1,3-butadiene, (B⁻) = 1-butene, *cis*-2-butene, *trans*-2-butene, (B) = butane. And the reaction network was shown in Figure 2.6.
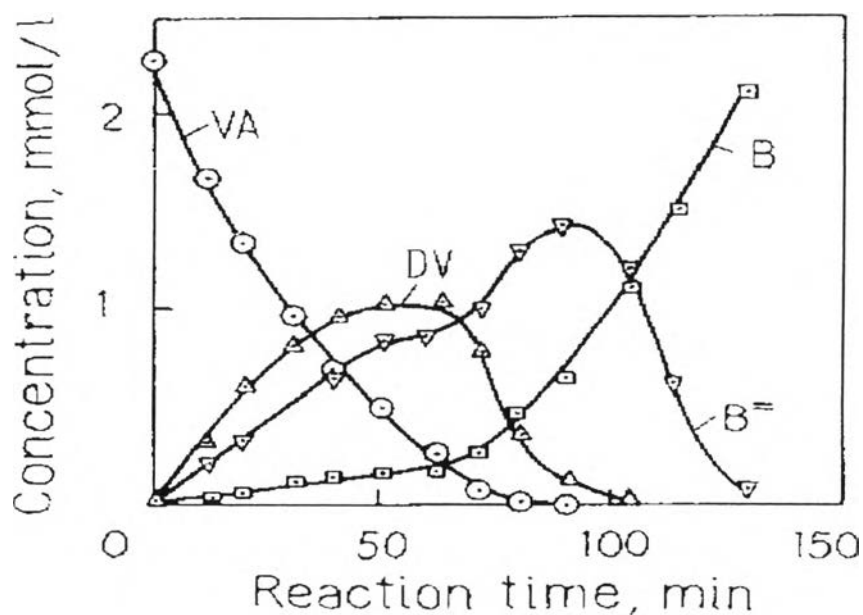

Figure 2.5: The plot of reaction mixture composition versus reaction time for 1.9% Pd/Al_2O_3 catalyst in gas-phase hydrogenation of vinyl acetylene. (Ryndin *et al.*, 1988)


Figure 2.6: The reaction network of vinyl acetylene hydrogenation. (Ryndin *et al.*, 1988)

Ardiaca *et al.* (2001) investigated the kinetic studies on egg-shell catalysts in case of liquid-phase hydrogenation of 1,3-butadiene and n-butenes on commercial Pd catalysts. They used three reactors which consist of slurry reactor, rotating-basket reactor and a recirculation system with an external fixed-bed reactor. They found that the slurry reactor had the problem of the catalyst dust adhesion at the vessel head so it was not considered. The rotating basket reactor had lower performance than the external fixed bed reactor as shown in the Figure 2.7. So they suggested that the external fixed bed reactor is the best reactor.
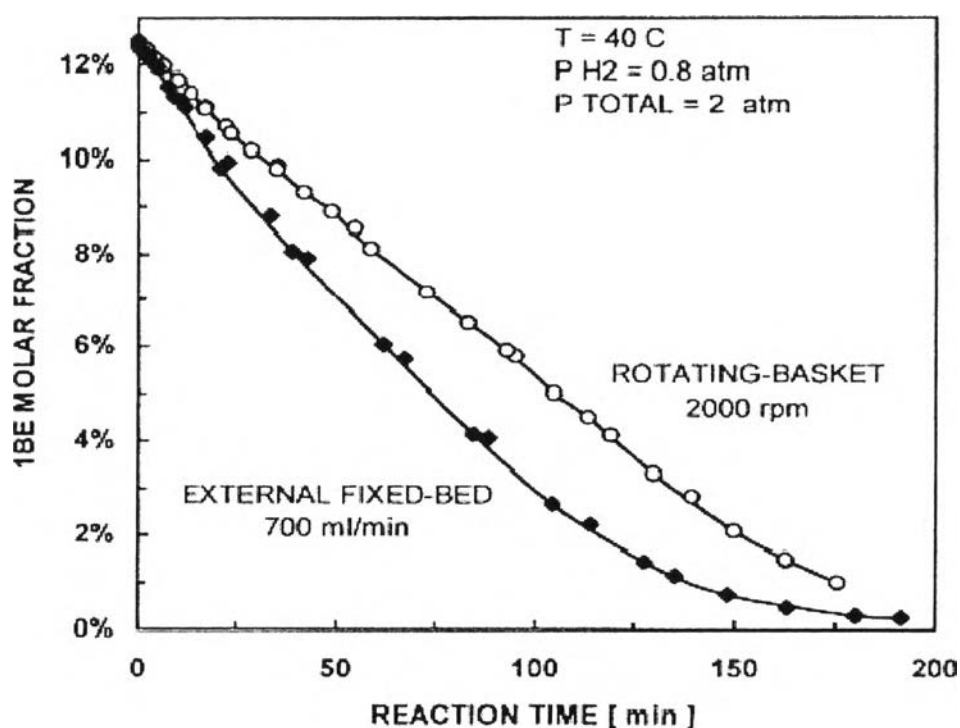

Figure 2.7: The consumption of 1-butene: comparison between the rotating-basket reactor and recirculation system with an external fixed-bed reactor. (Ardiaca *et al.,* 2001)

They found that the overall set of reactions of hydrogenation of butadiene taking place could be sketched as in Fig 2.8, where BD ≡ 1,3-butadiene, 1-BE ≡ 1-butene, cBE ≡ *cis*-2-butene, tBE ≡ *trans*-2-butene and BA ≡ *n*-butane. From the overall reaction network, butadiene could be hydrogenate to form 3 isomers of butene which were cBE, 1-BE and tBE. And all of these could be isomerized each other and could be further hydrogenated to form butane.
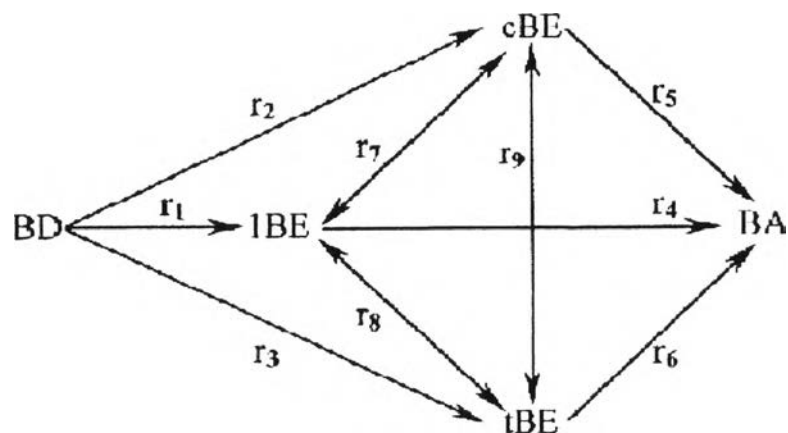
Figure 2.8: Overall reaction network of hydrogenation reaction of 1,3-butadiene. (Ardiaca *et al.*, 2001)

From the experimental data which exhibited in Fig 2.9 could be confirmed that the predicted reaction network was consistent with the experimental data.
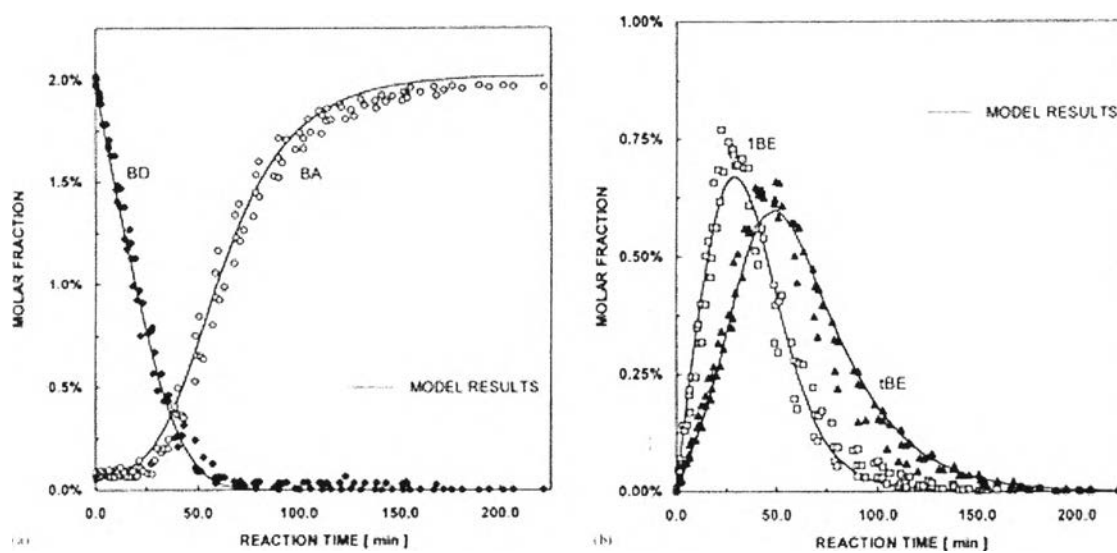

Figure 2.9: Comparison between predicted composition and experimental results of hydrogenated products as a function time. (Ardiaca *et al.*, 2001)

Meryer *et al.* (1963) studied the reaction between deuterium and 1-butyne, 1,2-butadiene and 1,3-butadiene on Pd/Al_2O_3. From the results, they found that 1-butyne would be hydrogenated to 1-butene, 1,2-butadiene would be hydrogenated to 1-butene, *cis*-2 butene and small amount of *trans*-2-butene and 1,3-butadiene would be hydrogenated to 1-butene, *trans*-2-butene and small amount of *cis*-2 butene. In 1- and 2-butyne and 1,2-butadiene, they suggested that the major reaction path involved adsorption with opening of one π-bond followed by successive reaction with an adsorbed H atom to give α-monoadsorbed butane which future reacted with an absorbed H atom to form butane. The reaction path in the hydrogenation of 1,3-butadiene involved none of above intermediates but probably adsorption as a largely π-adsorbed trans-butadiene followed by reaction with a absorbed H atom at carbon atom 4 to give an adsorbed allylic species which future reacted with a absorbed H atom at carbon atom 1 or 3.

Crespo-Quesada *et al.* (2011) studied the liquid-phase selective hydrogenation of 1-hexyne by using Pd/CNF/SMF reference catalyst and N-modified Pd catalyst. The hydrogenation reactions were carried out in a semi-batch stainless steel reactor. They claimed that the 1-hexyne would be hydrogenated to 1-hexene and 1-hexene could be further hydrogenated to *n*-hexane or could be isomerized to *cis*-2-hexene and *trans*-2-hexene. The hydrogenation reaction network of 1-hexyne could be written as shown in Figure 2.10.
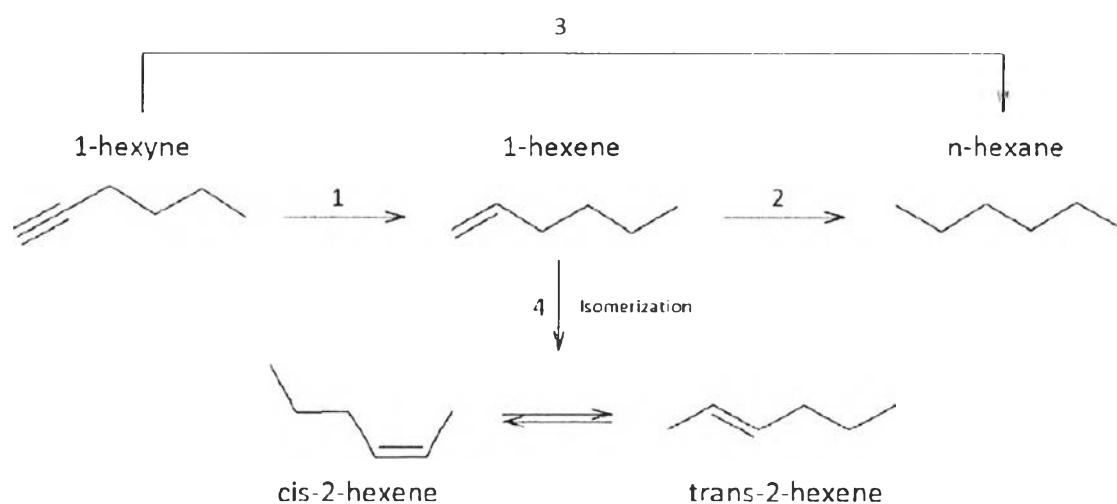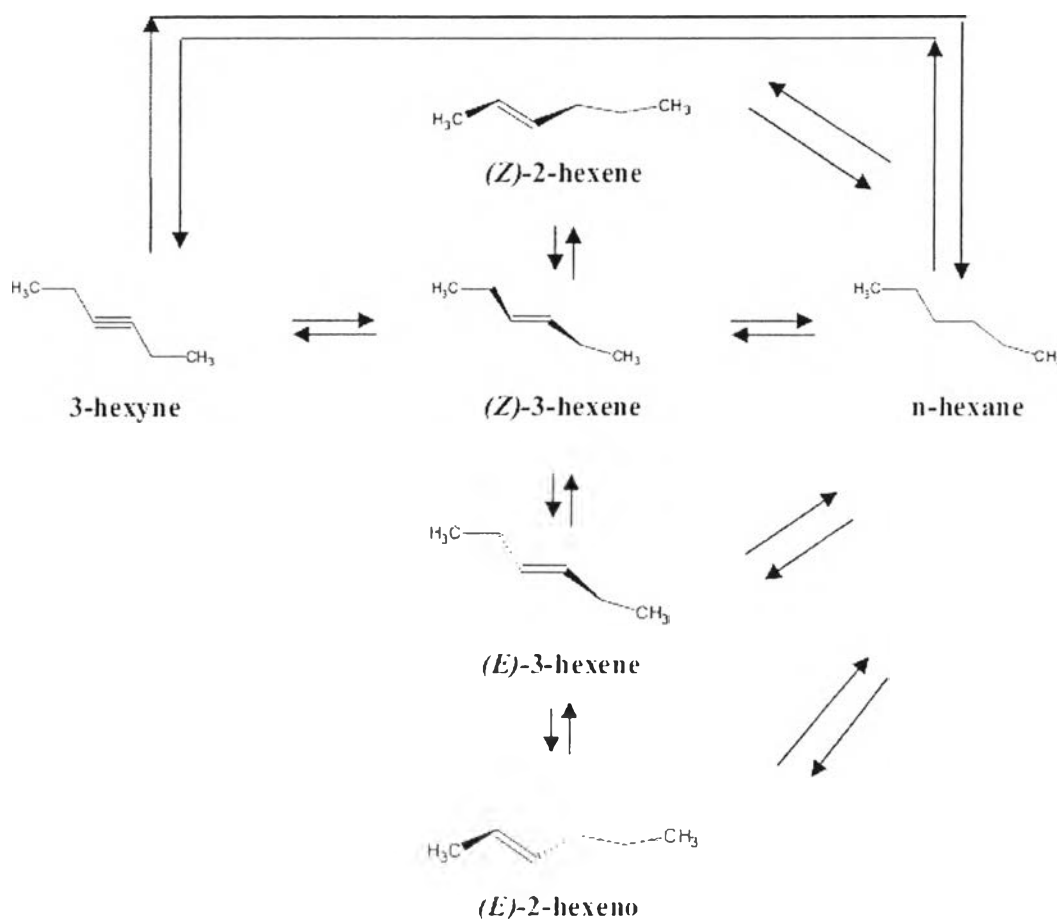

Figure 2.10: Hydrogenation reaction network of 1-hexyne.

Alvez-Manoli *et al.* (2010) studied the effect of mesostructured materials in the stereo-selective hydrogenation of 3-hexyne at 298 K and 40 psig pressure of H_2 over Pd-supported catalysts at different substrate: palladium (S:Pd) molar ratios. They claimed that the reaction would be zero order with respect to 3-hexyne concentration. And the starting 3-hexyne produces primarily *cis*-3-hexene, which subsequently is either hydrogenated to hexane or isomerized to *trans*-3-hexene and 2-hexenes that are found in very small amounts depending on the nature of the support used. The hydrogenation reaction network of 3-hexyne could be written as shown in Figure 2.11.
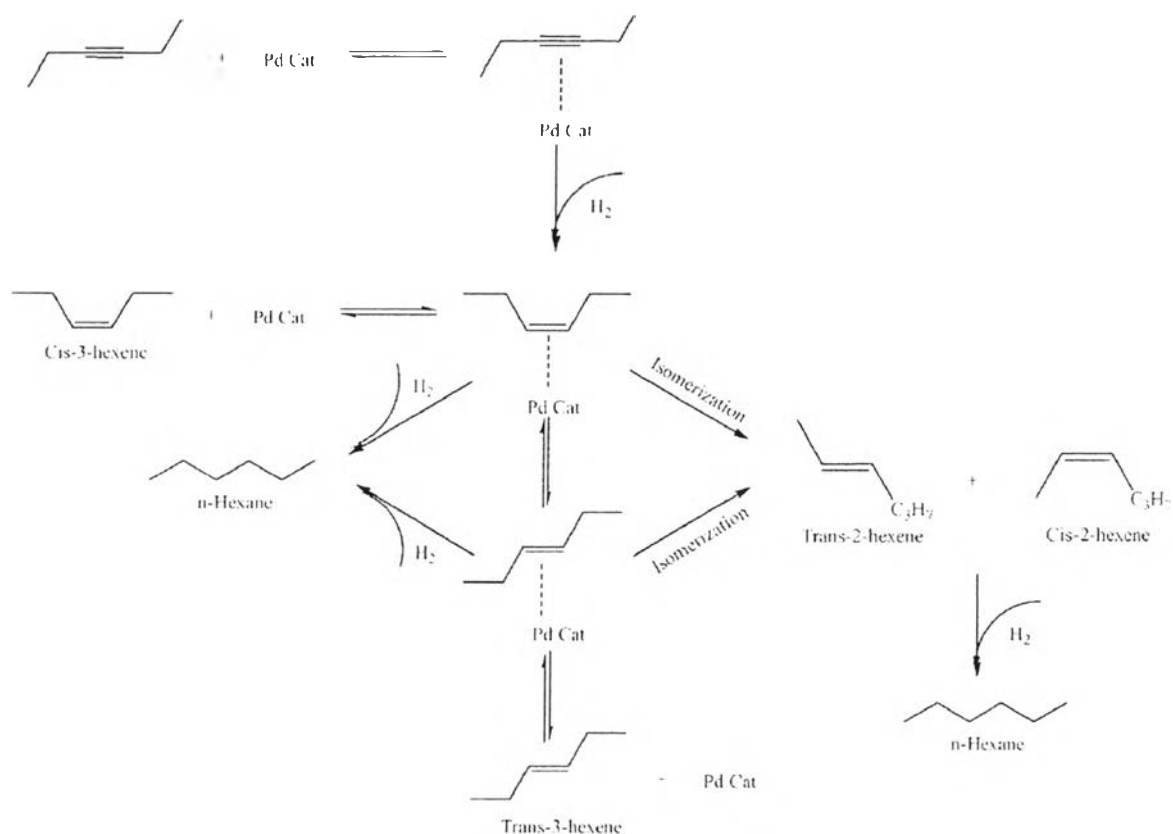
Figure 2.11: Hydrogenation reaction network of 3-hexyne.

Maccarrone *et al.* (2012) studied the partial hydrogenation of 3-hexyne over low-loaded palladium mono and bimetallic catalysts. Catalytic reaction tests were carried out in a stainless steel stirred tank batch reactor equipped with a magnetically coupled stirrer with two blades in counter-rotation under 1.4 bar of hydrogen pressure and 273-323 K reaction temperature. They suggested the possible kinetic mechanism of 3-hexyne hydrogenation could be written as shown in Figure 2.12.

Figure 2.12: Scheme of the 3-hexyne reversible hydrogenation reactions.

2.4 Catalyst for selective hydrogenation of acetylenic compound, butadiene and hexyne (1-hexyne, 2-hexyne and 3-hexyne)

The Pd catalyst has been successfully applied to selective hydrogenation process because of high activity at low temperature for hydrogenation of acetylenes and diolefins. However, there are many limitations such as the selectivity of Pd catalyst will be dropped at high acetylene conversion, isomerization of 1-butene rapidly occurs in the absence of 1,3-butadiene, Pd catalyst can be fouled by oligomerization of C_4 and Pd-based catalyst can be poisoned by COS, H_2S and some mercaptanes. From these reasons, the addition of second metal atom to Pd catalyst on various supports is the topic which is the alternative way to improve properties of catalyst for selective hydrogenation process.

Lederhos *et al.* (2011) studied the partial hydrogenation of hept-1-yne by using supported Pd and W as the catalysts. The catalysts they used were Pd and W monometallic catalysts and W-Pd and Pd-W bimetallic catalysts supported over alumina. The catalytic reaction tests were carried out in a stainless steel stirred tank batch reactor at 303 K and 150 kPa. From the results they found that W monometallic catalyst was an active but had the lowest selectivity to hept-1-ene in comparison to the bimetallic W-Pd catalysts. The addition of Pd to tungsten monometallic catalyst greatly improves the selectivity to desired product. However this improvement is found to decrease with the increase in the reduction temperature. And the reduction temperature is increased the total conversion of hept-1-yne is decreased. The Pd monometallic catalyst showed the high selectivity and the adding of W to Pd monometallic catalyst decrease the values of selectivity desired product. It can also be seen that as the reduction temperature is increased the selectivity of Pd-W catalysts is decreased. And the addition of W to Pd monometallic catalyst would increase total conversion 3.5 times. Finally, they summarized that the addition of a second metal to Pd and W monometallic catalysts to form Pd-W and W-Pd bimetallic catalysts would greatly improve both activity and conversion of hept-1-yne. And the W-Pd bimetallic catalysts reduced at 393K, was the most active and selective catalyst for partial hydrogenation of hept-1-yne.

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 catalysts was investigated in the gas-phase selective hydrogenation of 1,3-butadiene.They did the experiment by using 4 types of catalysts which consist of Pd/θ- Al_2O_3, Pd/α-Al_2O_3 and Pd/$(\theta$- $\alpha)$-Al_2O_3 which were 0.2%Pd on 100/0, 80/20, 40/60 and 0/100(%) θ/α-Al_2O_3. The mixed-phases alumina supports in this study were prepared by calcination of bayerite, $(Al(OH)_3)$ at 1100–1120 °C for 180 min. The pure θ- and α-Al_2O_3 were obtained by calcination of bayerite at 960 °C and 1200 °C, respectively for 180 min. They found that increasing of α-phase affected to the properties of Alumina such as decreasing the Pd active sites, %Pd dispersion, acidity and the increasing of α-phase will be increased the Pd° particle size and created the larger particle/size of α-phase, low surface area, large pore size distribution and small pore volume. The increasing of θ-phase will be affected to the properties of alumina also such as increasing the acidity, Pd activity, %Pd dispersion, pore volume and will be created the narrow pore size distribution, small particle size of θ-phase, high surface area and decreased the Pd° particle size. From this result, they conclude that Pd supported on 80% θ- and 20% α-Al_2O_3 had the best performance because it exhibited both low loss of 1-butene product and low butane 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/Al_2O_3, 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/Al_2O_3 bimetallic catalysts. Beside the hydrogenated products, 1-1-diethoxy-2-hexene (Acetal) was formed in a small quantity. From this result, they conclude that Pd-Co/Al_2O_3 showed the highest activity among the catalysts tested.

Furlong *et al.* (1994) studied the vapor phase selective hydrogenation of 1,3-butadiene in 1-butene over alumina supported Pd and Pd-Cu catalyst in both batch and plug flow reactor. The reaction study was carried out in plug flow reactor at 288-313 K and atmospheric pressure. From the results, they found that Pd-Cu/Al_2O_3 catalyst was more selective and active than Pd/Al_2O_3 catalyst because the addition of

Cu to supported Pd catalysts greatly improves their selectivity for hydrogenating 1,3-butadiene directly to *n*-butenes without hydrogenating or isomerizing the 1-butene.

Sarkany *et al.* (2002) studied the hydrogenation of acetylene over low loaded Pd and Pd-Au/SiO$_2$ catalysts. The reaction study was carried out in an atmospheric pulse-flow reactor. They did the experiment by using 4 type of catalysts which consist of 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$_2$. From the results, they found that the Pd-Au/SiO$_2$ would show both lower over-hydrogenation and lower C4 formation than Pd/SiO$_2$. They summarized that the addition of Au would reduce ethane formation (improve ethane selectivity) and the carbon coverage.

Ngamsom *et al.* (2004) studied the effect of pretreatment with NO and N$_2$O to characterizations of Pd-Ag/Al$_2$O$_3$ which was used as a catalyst for selective acetylene hydrogenation. They found that nitrate or nitrite species from NO and N$_2$O pretreatment would strongly adsorb on Pd surface and this nitrate or nitrite species which adsorbed on Pd would block the Pd sites responsible for direct ethane formation. It increased the ethylene selectivity.

Pattamakomsan *et al.* (2010) studied the gas phase selective hydrogenation of 1,3-butadiene over Pd and Pd-Sn catalysts supported on different phases of alumina. (mixed phase □/α- and pure α-alumina). From the experiment, the catalysts they used consist of 0.5wt% Pd/pure α- Al$_2$O$_3$, 0.5wt% Pd/mixed phase *(θ/α)*-Al$_2$O$_3$, 0.5wt% Pd-0.2wt% Sn/ pure α- Al$_2$O$_3$ and 0.5wt% Pd-0.2wt% Sn/mixed phase *(θ/α)*-Al$_2$O$_3$. The reaction study was carried out in fixed-bed reactor at 30-70°C and atmospheric pressure. They found that the nanoparticles of Pd and Pd- Sn supported on mixed phase *(θ/α)*-Al$_2$O$_3$ would be homogeneous. On the other hand, nanoparticles of Pd and Pd- Sn supported on pure α- Al$_2$O$_3$ would not be homogeneous and the bimetallic nanoparticles on mixed phase *(θ/α)*-Al$_2$O$_3$ much more homogeneous than another one and they provided the highest conversion. Adding of tin would not only modify electronic property of Pd catalyst, dilute the Pd surface atoms but also will suppress the butane formation and isomerization of 1-butene. From this result, they conclude that Pd-Sn supported on mixed phase alumina catalyst was the best catalyst which had both good selectivity and 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 Al_2O_3 and β-zeolite as a catalyst. From the results, they found that Pd-Ag/Al_2O_3 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/Al_2O_3 catalysts and Pd/Al_2O_3 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-Al_2O_3 counterparts, the Pd/ Na^+-β-zeolite, Pd-Ni/Na^+-β-zeolite showed higher hydrogenation activities than those on the Pd/Al_2O_3, Pd-Ni/Al_2O_3. Although hydrogenation activity of Pd-Ag/ Na^+-β-zeolite is lower than Pd-Ag/Al_2O_3.

Desiderio *et al.* (1975) mentioned a patent about selective hydrogenation of vinyl-acetylene. In the experiment, they studied the hydrogenation of the mixture of 0.7-1.0 %vinyl-acetylene in butadiene. The reactors they used are 2 packed-bed reactors which packed by 0.05-0.2%palladium on alumina. They investigated the hydrogenation in both mixed phase condition (pressure 6-8 atm and temperature 40-60 °C) and liquid phase condition (pressure 20 atm). From the results, they found that the vinyl-acetylene hydrogenation in mixed phase condition had greater vinyl-acetylene conversion and 1,3-butadiene selectivity than vinyl-acetylene hydrogenation in liquid phase condition.

Beamson *et al.* (2011) studied the selective hydrogenation of amides using bimetallic Ru/Re and Rh/Re catalysts. They found that Ru/Re and Rh/Re catalysts were effective for the liquid phase hydrogenation of cyclohexanecarboxamide ($CyCONH_2$) to $CyCH_2NH_2$ in up to 95% selectivity without the requirement for ammonia to inhibit secondary and tertiary amine formation. Variation in Ru:Re and Rh:Re composition result in only minor changes in product selectivity with no evidence of catalyst deactivation at higher levels of Re. And they also claimed that Rhenium-based catalysts had received greater attention than other metals for the

reduction of 'difficult' functional groups such as amides, and particularly carboxylic acids and esters.

Wongwaranon *et al.* (2008) studied the selective hydrogenation of acetylene by using Pd catalysts supported on nanocrystalline α-Al$_2$O$_3$ and Ni-modified α-Al$_2$O$_3$ which was prepared by sol-gel and solvothermal methods as a catalyst. From the results, they found that both catalytic performances of the Pd catalysts supported on nanocrystalline α-Al$_2$O$_3$ and Ni-modified α-Al$_2$O$_3$ in selective hydrogenation of acetylene had higher performances than Pd catalysts supported on commercial α-Al$_2$O$_3$. Ethylene selectivities were improved in the order: Pd/Ni-modified α-Al$_2$O$_3$-sol-gel > Pd/Ni-modified α-Al$_2$O$_3$-solvothermal = Pd/α-Al$_2$O$_3$-sol-gel > Pd/α-Al$_2$O$_3$-solvothermal >> Pd/α-Al$_2$O$_3$- commercial. And they suggested 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.

Koussathana *et al.* (1991) studied the Slurry-phase hydrogenation of aromatic compounds over monometallic (Pt, Rh, Ru) and bimetallic (Pt, Rh, Ru-Pd, Ir, Re) catalysts supported on γ-Al$_2$O$_3$ or TiO$_2$. The reaction study was carried out in a three-phase slurry reactor at a temperature of 300 °C and a hydrogen pressure of 66 atm. Under the conditions employed in this study they found that, the bimetallic formulations exhibited significantly higher hydrogenation activity as compared to their monometallic counterparts. The enhancement factor was found to be larger when the bimetallic formations were supported on TiO$_2$ as opposed to Al$_2$O$_3$ carriers. Bimetallic catalysts, especially those containing rhenium (Re) were also found to exhibit enhanced resistance to sulfur poisoning.
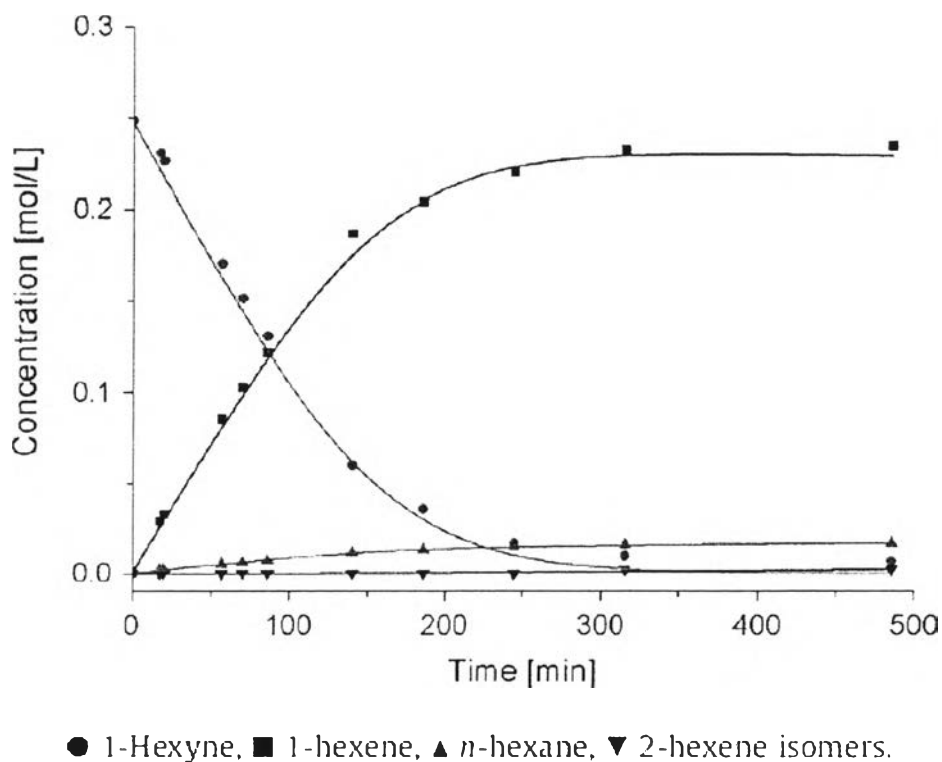
Alvez-Manoli *et al.* (2010) studied the effect of mesostructured materials in the stereo-selective hydrogenation of 3-hexyne at 298 K and 40 psig pressure of H$_2$ over Pd-supported catalysts at different substrate: palladium (S:Pd) molar ratios. They found that the Pd supported on mesostructured solids are effective catalysts for the stereo-selective hydrogenation of 3-hexyne to *cis*-3-hexene in toluene. The most active catalyst was 1% Pd/SBA-15 in comparison to 1% Pd/MSU-γ, 1% Pd/MCM-48 and commercial 1% Pd/Al$_2$O$_3$ catalysts.

Crespo-Quesada *et al.* (2011) studied the liquid-phase selective hydrogenation of 1-hexyne by using Pd/CNF/SMF reference catalyst and N-modified Pd catalyst. The hydrogenation reactions were carried out in a semi-batch stainless steel reactor. They found that the N-modified Pd nanoparticles were significantly more selective (up to 98.5% at 25% conversion) than reference catalyst with non-modified Pd nanoparticles on the same support (88%). Moreover, the high selectivity was maintained up to full conversion, and thus, the over-hydrogenation toward the alkane was completely suppressed due to a site-blocking effect of the N-containing ligands. And the imidazolium-functionalized biby ligand was found to interact more strongly with the nanocarbon support reinforcing Pd anchoring and reducing leaching in to the liquid media.


● 1-Hexyne, ■ 1-hexene, ▲ *n*-hexane, ▼ 2-hexene isomers.
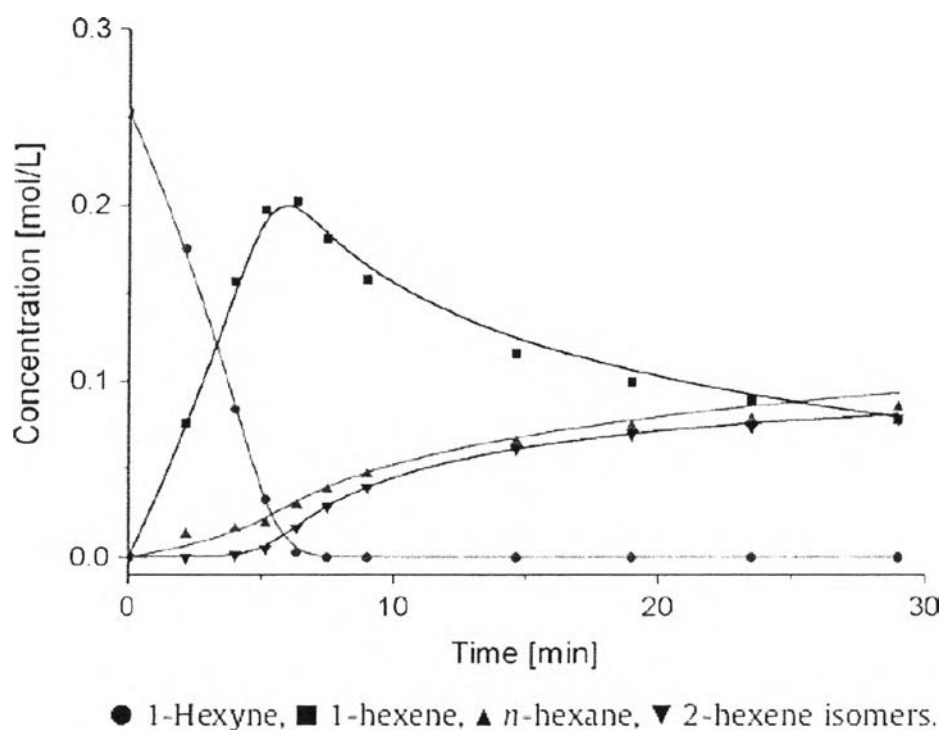
Figure 2.13: Experimental points and kinetic curves modeled for the reference catalyst.

● 1-Hexyne, ■ 1-hexene, ▲ n-hexane, ▼ 2-hexene isomers.

Figure 2.14: Experimental points and kinetic curves modeled for the N-modified Pd catalyst.

Maccarrone *et al.* (2012) studied the partial hydrogenation of 3-hexyne over low-loaded palladium mono (Pd/A) catalyst, bimetallic (PdNi/A and WPd/A) supported on γ-alumina catalysts and Lindlar catalyst. Catalytic reaction tests were carried out in a stainless steel stirred tank batch reactor equipped with a magnetically coupled stirrer with two blades in counter-rotation under 1.4 bar of hydrogen pressure and 273-323 K reaction temperature. They found that bimetallic catalysts showed higher activities and very similar selectivities (>93%) than the monometallic system and further than Lindlar catalyst. The rank of activity order is: WPd/A>PdNi/A>Pd/A>>Lindlar. Furthermore, All catalysts are active in the range of temperatures studied, 273-323 K, even at the lowest temperature.
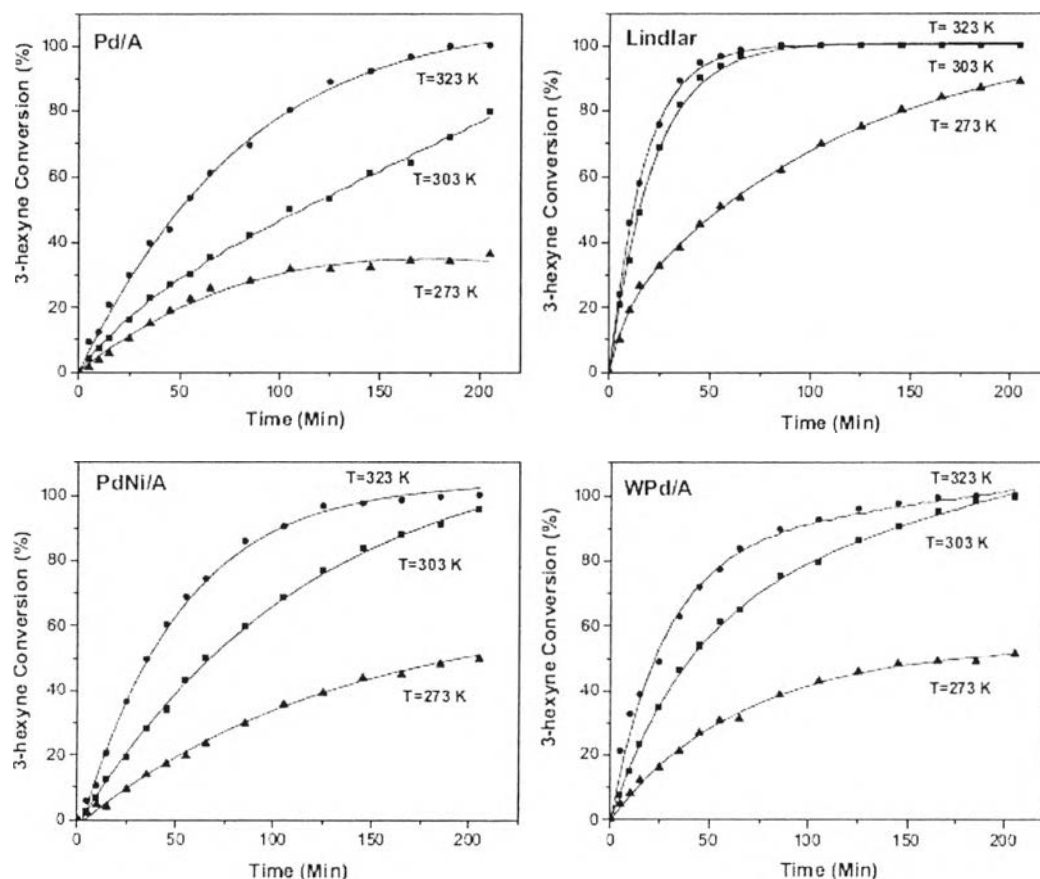
Figure 2.15: 3-Hexyne total conversion (%) as a function of time for Pd/A, Lindlar, PdNi/A and WPd/A catalysts, measured at 1.5 bar and different temperatures: T1 = 273 K (▲), T2 = 303 K (■) and T3 = 323 K (●).

Anderson *et al.* (2009) studied the hydrogenation of 1-hexyne and 2-hexyne by using Pd catalyst modified by Bi and Pb. In case of 1-hexyne hydrogenation they found that Bi had little effect on the rate of the 1-hexyne hydrogenation, the rate of subsequent reactions of the 1-hexene formed were suppressed. On the other hand, the addition of Pb did not yield the benefits which were gained by addition of Bi to Pd catalyst in terms of reducing the rate of 1-hexene conversion without suppressing its rate of formation. In this case, Bi was a more effective modifier than Pb. The addition of Bi did not modify Pd particle size. And increasing the contact time between Pd catalyst and Bi solution increased the amount of residual deposited Bi. In case of 2-hexyne hydrogenation, Bi is a poor modifier and fails to suppress reactions of *cis*-2-hexene. Pb on the other hand, has a significant impact in terms of suppressing reactions of *cis*-2-hexene.

2.5 Catalyst deactivation during hydrogenation reaction

Catalyst deactivation is defined as a phenomenon in which the structure and state of the catalyst change, leading to the loss of active sites on the catalyst's surface and thus causing a decrease in the catalyst's performance.

In general, heterogeneous catalyst deactivation can be occurred during the hydrogenation reaction. Many causes make the catalyst deactivated such as poisoning, fouling, coking, carbon deposition, thermal degradation, vapor formation, corrosion/leaching, attrition and crushing. In the liquid phase hydrogenation reaction of vinyl acetylene-rich mixed C4 and 1-hexyne has mostly used Pd/Al_2O_3 as a catalyst, the deactivation mainly occur from poisoning, coking, and Pd leaching.

2.5.1 Poisoning

The poisoning of heterogeneous catalysts occurs as a result of the adsorption of the poison or the product of its chemical transformation on the surface of the catalyst and cause the effectiveness of catalyst decreases. The poison affects to the catalytic activity by several mechanisms. The first mechanism is physically blocking the circumstance reaction sites (geometric effect). The second is electronically modifying with the neighbor atoms to changing the adsorption ability (electronic effect). The third is the restructuring of the surface by very strongly adsorption. The possible poison compounds of Pd catalyst for hydrogenation reaction are CO, S, Pb, CS_2, thiophene, NO, N_2O and H_2S. The poisoning may be temporary or permanent. For example, during the synthesis of ammonia on an iron catalyst, oxygen and its derivatives temporarily poison Fe. In this case, the surface of the catalyst is freed of oxygen under the action of a pure $N_2 + H_2$ mixture and the degree of poisoning is reduced. Sulfur compounds permanently poison Fe, since the activity of the catalyst is not successfully reduced by the action of the pure mixture. Thorough purification is required to prevent poisoning of the reacting mixture that passes onto the catalyst.

2.5.2 Coke formation

It implies many successive chemical transformations of reactant molecules. It can be viewed as the high molecular weight hydrocarbon condensed on catalyst surface. In mixed C4 hydrogenation, coke can be generated from the polymerization of unsaturated hydrocarbon as vinyl acetylene and butadiene. Coke can act as both physical blockage of the active site and poison of catalyst. However, a certain amount of carbon deposited is required for the selective hydrogenation of acetylene to ethylene.

2.5.3 Leaching

The leaching is loss of valuable metal by formation of soluble complex compounds may occur. Leaching of active species particularly occurs during the liquid phase synthesis of fine chemicals. The nitro compound 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 palladium in a well-reduced.

Origin	Mechanism	Examples
Poisoning	Chemisorption (or reaction) of feed impurities or reaction products on the active sites, limiting or inhibiting reactant chemisorption Reversible or irreversible	*Metals:* S compounds, CO, polyaromatics, coke *Acid oxides:* bases, polyaromatics, coke
Fouling and coking	Deposit of heavy compounds: feed impurities or secondary products (coke) on the active surface Only reversible by oxidative regeneration	*Metals:* coke (e.g. Pt), carbon (e.g. Ni) *Acid oxides:* FCC: deposit of heavy feed components, catalytic or thermal coke
Leaching	Loss of active component, e.g. by dissolution in reaction medium Most common in liquid-phase fine chemicals synthesis Often reversible	e.g. dissolution of metal framework (e.g. Cr in CrS-1) component of metallosilicate molecular sieves

Figure 2.16: Deactivation of solid catalysts: Poisoning, Fouling and Coking, Leaching.