CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Mixed C4 Hydrocarbons

Mixed C4 hydrocarbons which are a product from fluid catalytic cracking unit (FCC) in petrochemical process are a mixture of hydrocarbons with 4 carbon atoms in its molecule, such as butadienes, butenes, butanes, isobutylene and C4-acetylenes. The typical composition of mixed C4 stream from fluid catalytic cracking unit is shown in Table 2.1.

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

Many compounds in mixed C4 are economically valuable, since they can be used as raw materials in many downstream processes. For instance, 1,3-butadiene is used for polybutadiene and styrene-butadiene rubber production, 1-butene is used as a co-monomer to produce linear low density polyethylene (LLDPE), isobutylene is used for producing methyl *tert*-butyl ether (MTBE) or ethyl *tert*-butyl ether (ETBE) and butane is used as the liquefied petroleum gas (LPG). The other low value C4-hydrocarbons, like C4-acetylene, 2-butene and 1,2-butadiene will be eliminated or transformed to higher value hydrocarbons.

Typically, the separation and purification of the mixed C4 hydrocarbons, the mixed C4 stream from fluid catalytic cracking unit is sent to a butadiene extraction process in order to extract and purify 1,3-butadiene at the beginning. C4-acetylenes are removed from the mixed C4 stream to prevent peroxide production and self-explosion since it is very reactive. The raffinate stream from the butadiene extraction process mainly contains butenes and butanes but it is still composed of a small amount of 1,3-butadiene and has to be recovered before sending to downstream process by hydrogenation process. Furthermore, the hydrogenation process can be also used to hydrogenate 1,3-butadiene in the mixed C4 stream to 1-butene and improve low value hydrocarbons like C4-acetylene to higher value hydrocarbons, such as 1,3-butadiene or 1-butene. The raffinate-1 which is an outlet stream from hydrogenation process will be fed to etherification process in order to produce the ether products, such as methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE), from isobutene in the raffinate-1 steam. Finally, the raffinate-2 which is a byproduct stream from etherification process will be fed to 1-butene process in order to purify 1-butene from the raffinate-2 stream and the raffinate stream from this process can be used as liquefied petroleum gas (LPG).
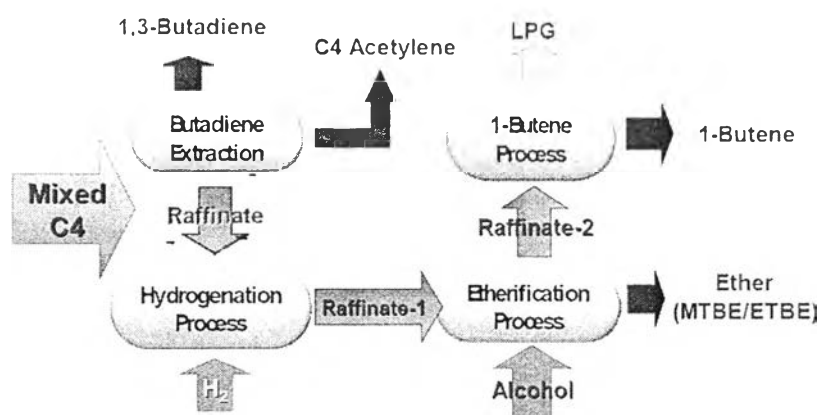

Figure 2.1 The diagram of the typical C4 separation and purification plant (Choocheun, 2012).

2.2 Hydrogenation

Hydrogenation reaction which is a chemical reaction about the addition of hydrogen atoms to the unsaturated compounds or molecules reduces double or triple bonds in the hydrocarbon molecules. Hydrogenation is broadly used in many applications, such as synthesis and manufacture of fine and industrial chemicals.
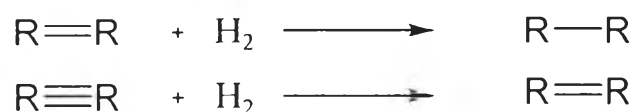
$$R{=}R \ + \ H_2 \longrightarrow \ R{-}R$$
$$R{\equiv}R \ + \ H_2 \longrightarrow \ R{=}R$$

Figure 2.2 Hydrogenation reaction of unsaturated hydrocarbon.

2.2.1 Hydrogenation of C4-C6 Hydrocarbons

Ryndin *et al.* (1988) studied the gas-phase hydrogenation of vinylacetylene by using Pd/SiO_3 and $Pd/\gamma\text{-}Al_2O_3$ as the catalysts. The possible reaction is shown in Figure 2.3 and the result from reaction study is shown in Figure 2.4 and. They suggested that butadiene (DV) and butenes ($B^=$), a mixture of 1-butene, *cis*- and *tran*-2-butene, were formed by the hydrogenation of vinylacetylene (VA). Moreover, butadiene could be hydrogenated to form butenes and, finally, butane (B).
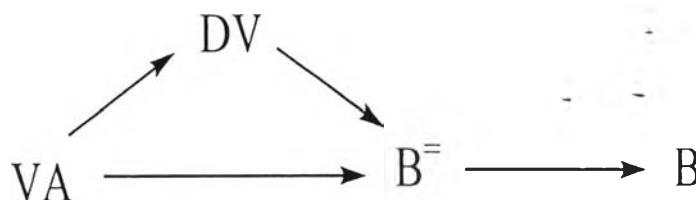

Figure 2.3 The possible reaction of vinyl acetylene hydrogenation (Ryndin *et al.*, 1988).
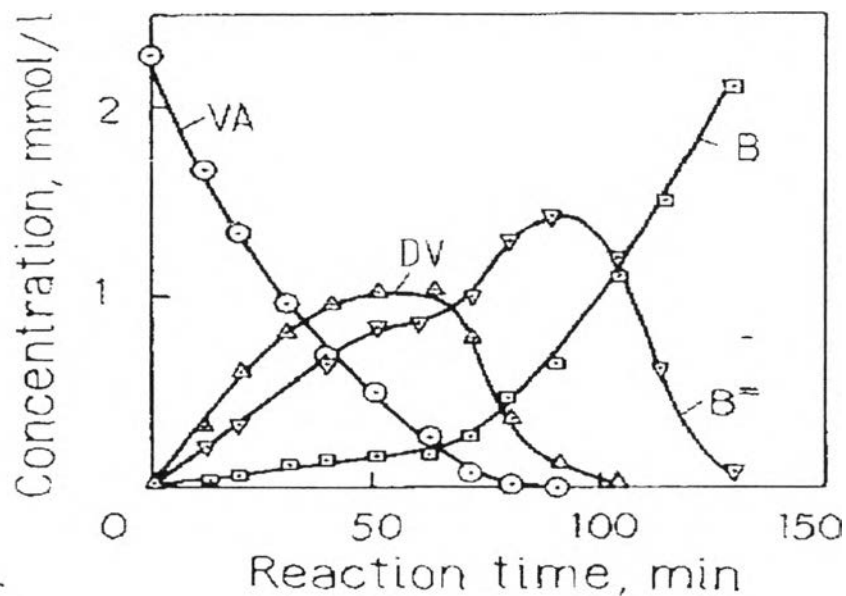
Figure 2.4 The plot of reaction mixture composition versus reaction time for 1.9% Pd/Al$_2$O$_3$ catalyst in gas-phase hydrogenation of vinyl acetylene (Ryndin *et al.*, 1988).

Ardiaca *et al.* (2001) studied the kinetics of liquid-phase hydrogenation of 1,3-butadiene and *n*-butenes on commercial Pd/Al$_2$O$_3$ catalysts of the egg-shell type by using three types of the reactor, 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 the butadiene hydrogenation is shown in Figure 2.5. From this reaction network, butadiene was hydrogenated to the three isomers of butene and they could be isomerized to each other and, finally, butane. Moreover, they found that the slurry reactor was not considered because it had diffusion limitations in using a small particle size of catalyst. The rotating basket reactor was slower rate than the external fixed bed reactor as shown in the Figure 2.7. It could be ascribed to relatively low liquid flow through the basket. They concluded that the external fixed bed reactor is the best reactor compared to the others which they studied.
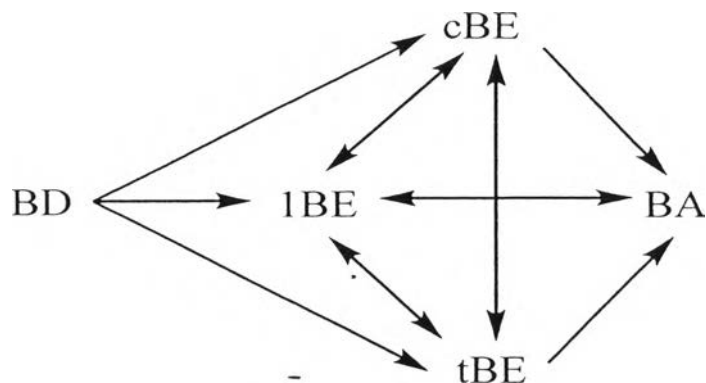
Figure 2.5 Overall reaction network of hydrogenation reaction of 1,3-butadiene, where BD ≡ 1,3-butadiene, 1-BE ≡ 1-butene, cBE ≡ *cis*-2-butene, tBE ≡ *trans*-2-butene and BA ≡ *n*-butane (Ardiaca *et al.*, 2001).
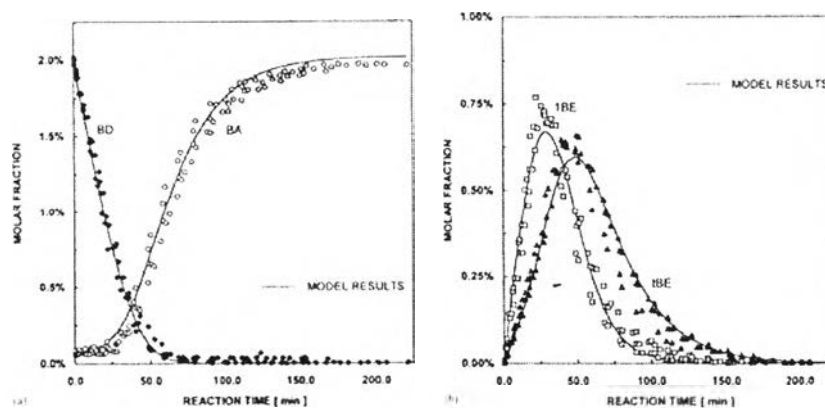

Figure 2.6 Comparison between predicted composition and experimental results of hydrogenated products as a function time (Ardiaca *et al.*, 2001).

Grant *et al.* (1976) studied the hydrogenation of 1,2-butadiene over nickel powder, nickel-alumina and nickel-silica. They found that almost of 1,2-butadiene were hydrogenated to butenes. Furthermore, 1,2-butadiene is accompanied by slowly isomerized to 1,3-butadiene.
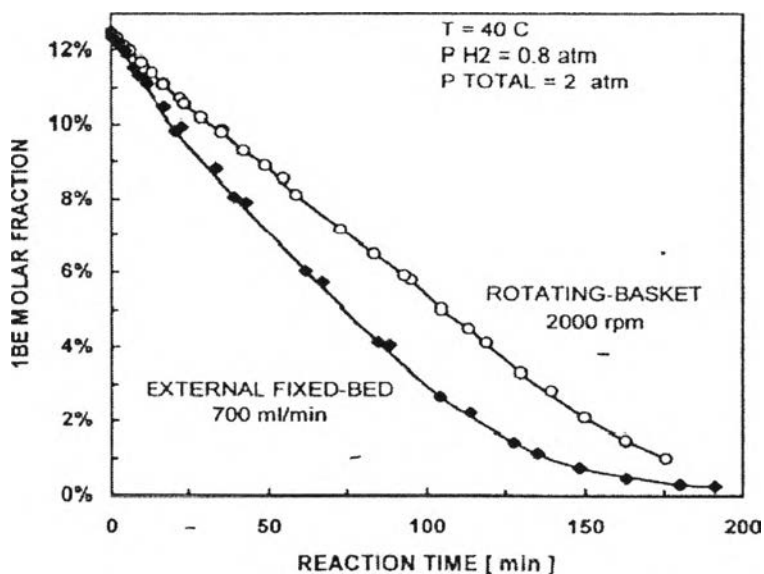
Figure 2.7 The consumption of 1-butene: comparison between the rotating-basket reactor and recirculation system with an external fixed-bed reactor (Ardiaca *et al.*, 2001).

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 used for this experiment were 1-butene, isobutene or butadiene and a 5 wt% of butadiene in isobutene. They found that the hydrogenation of 1-butene produced *cis*- and *trans*-2-butene and *n*-butene. The hydrogenation of isobutene produced isobutane. When the mixture of 1,3-butadiene and isobutene was used as a starting reactant, isobutane, 1-butene, 2-butene and *n*-butane were the products. From these results, they concluded that isobutane is the only product for the hydrogenation of isobutene. Therefore, the hydrogenation of isobutene which is shown in Figure 2.8 could be excluded from the reaction network of 1,3-butadiene hydrogenation.

Alves *et al.* (2007) studied the liquid-phase hydrogenation of 1-butyne over palladium/alumina catalyst by using recirculation system with an external fixed-bed reactor. They found that 1-butene was the only product of the 1-butyne

hydrogenated until 1-butyne reached a high conversion. For longer reaction times, 1-butene reacted to produce n- butane, *cis-* and *trans-*2-butene as shown in Figure 2.9.
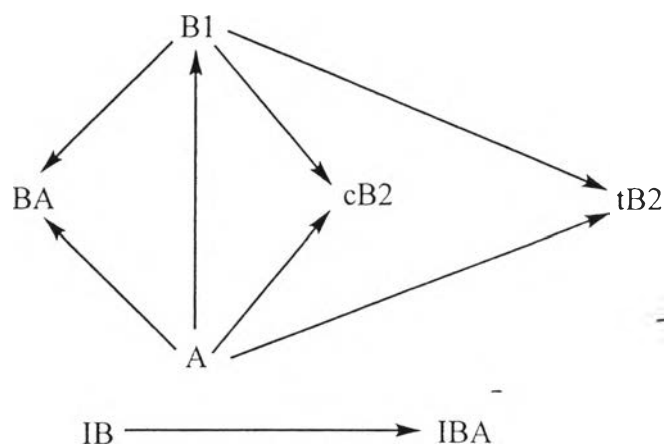

Figure 2.8 The reaction network of hydrogenation of 1,3-butadiene and isobutene, where A≡ 1,3-butadiene, B1≡ 1-butene, cB2≡ *cis*-2-butene, tB2≡ *trans*-2-butene, BA≡ n-butane, IB≡ isobutene, IBA≡ isobutane (Seth *et al.*, 2007).
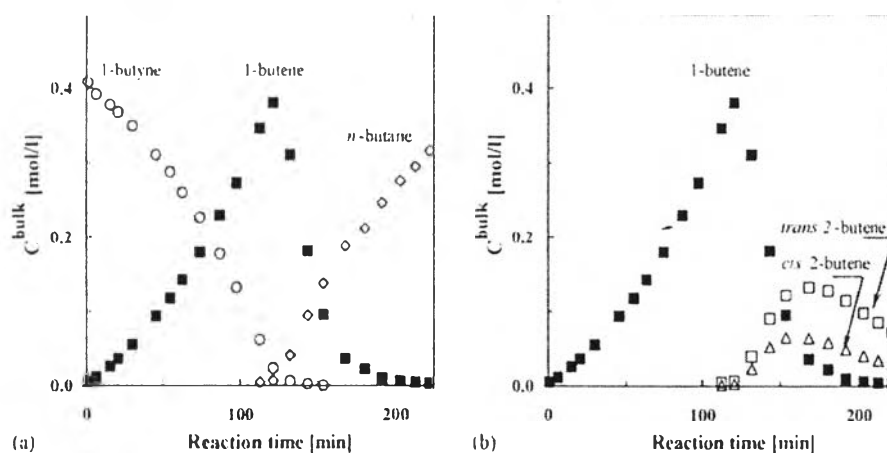

Figure 2.9 Variation of hydrocarbon bulk concentrations with reaction time (Alves *et al.*, 2007).

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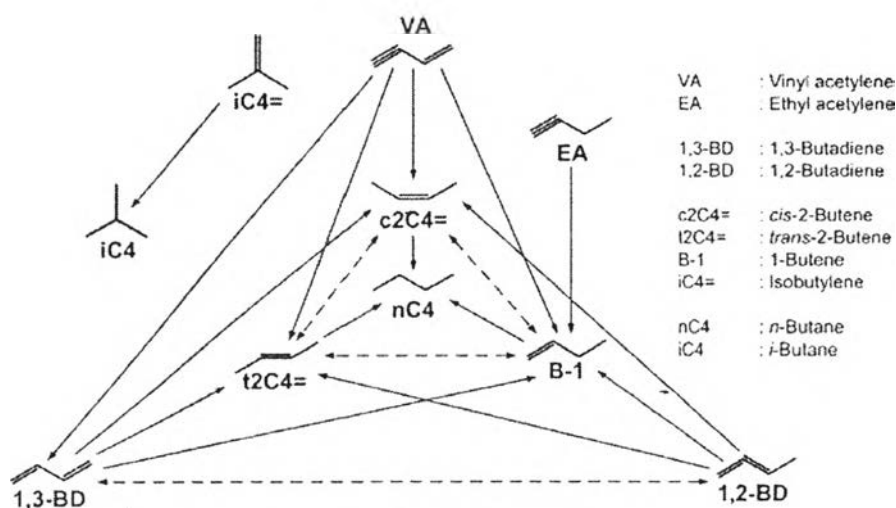

Figure 2.10 The possible reaction of hydrogenation of C4-hydrocarbon (Choocheun, 2012).

Meryer *et al.* (1963) studied the reaction between deuterium and 1-butyne, 1,2-butadiene and 1,3-butadiene on palladium/alumina catalyst. They found that 1-butyne produced 1-butene, 1,2-butadiene produced 1-butene, *cis*-2 butene and a small amount of *trans*-2-butene and 1,3-butadiene produced to 1-butene, *trans*-2-butene and a small amount of *cis*-2-butene.

Crespo-Quesada *et al.* (2011) studied the liquid-phase selective hydrogenation of 1-hexyne by using palladium/carbon nanofiber/sintered metal filter reference catalyst and nitrogen-modified palladium catalyst. The hydrogenation reactions were achieved in a semi-batch stainless steel reactor. They suggested that 1-hexyne could be hydrogenated to 1-hexene. The *n*-hexane formation was occurred not only by hydrogenation of 1-hexene to *n*-hexane but also by hydrogenation of 1-hexyne to *n*-hexane directly. Moreover, 1-hexene could be isomerized to *cis*-2-hexene and *trans*-2-hexene. The hydrogenation reaction network of 1-hexyne is written as shown in Figure 2.11.
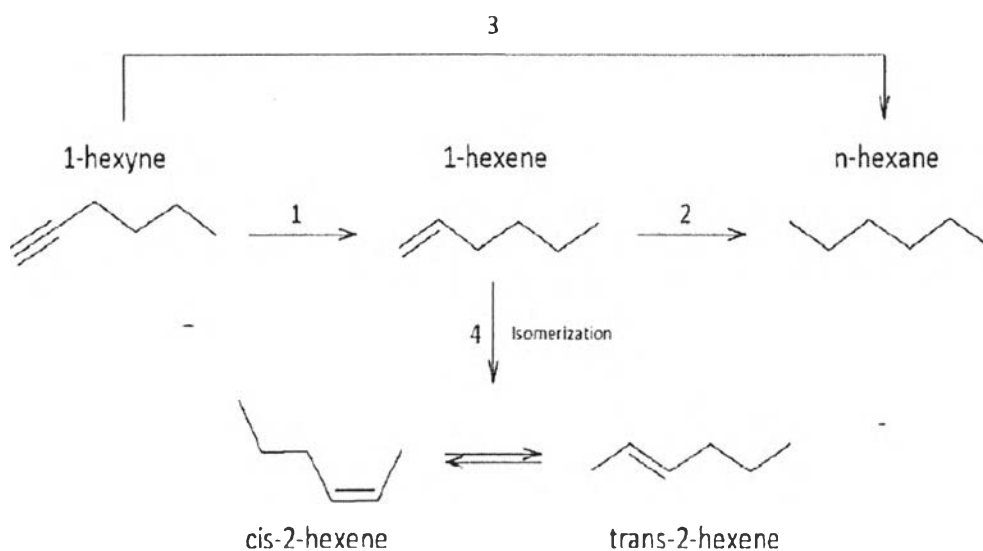
Figure 2.11 Hydrogenation reaction network of 1-hexyne (Crespo-Quesada *et al.*, 2011).

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. They suggested that the reaction would be zero order with respect to 3-hexyne concentration. The starting 3-hexyne produced primarily *cis*-3-hexene, and hydrogenated to hexane or isomerized to *trans*-3-hexene and 2-hexenes. The hydrogenation reaction network of 3-hexyne is written as shown in Figure 2.12.

Maccarrone *et al.* (2012) studied the partial hydrogenation of 3-hexyne over low-loaded palladium mono and bimetallic catalysts. Catalytic reaction tests were occurred in a stainless steel stirred tank batch reactor. They suggested that the hydrogenation reaction network of 3-hexyne is written as shown in Figure 2.13.
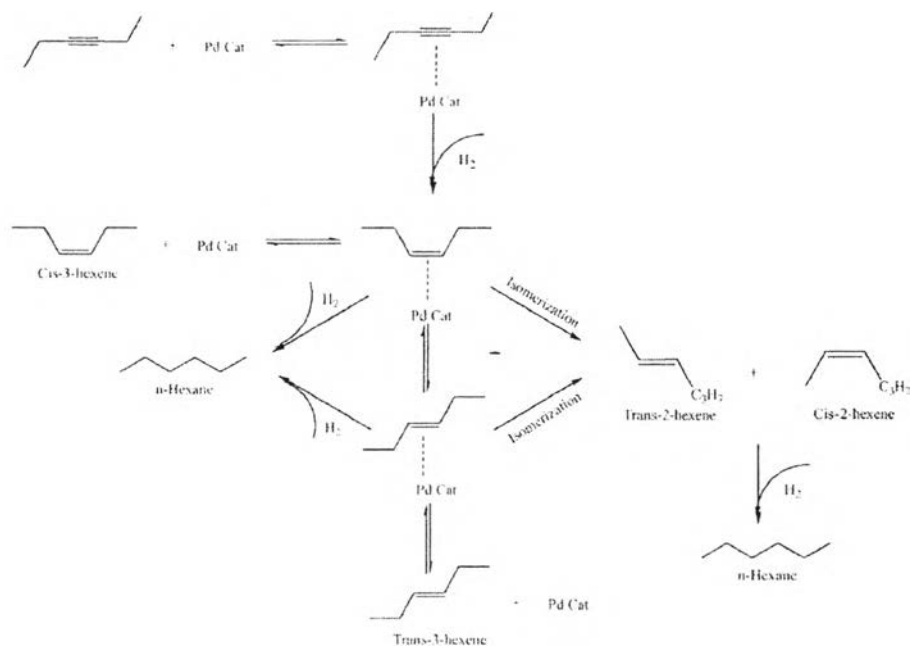
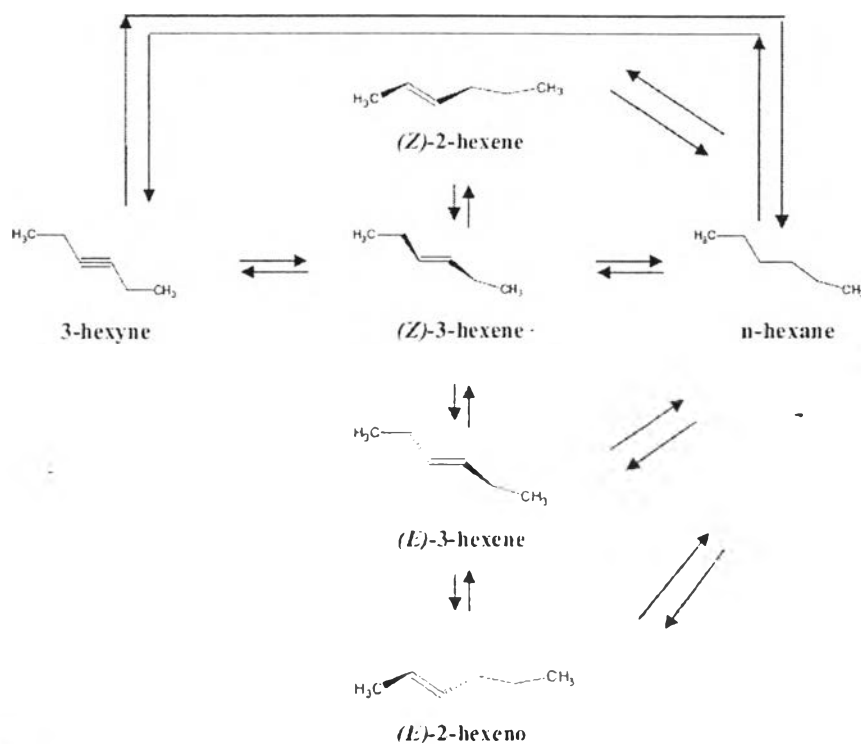**Figure 2.12** Hydrogenation reaction network of 3-hexyne (Alvez-Manoli *et al.*, 2010).

Figure 2.13 Scheme of the 3-hexyne reversible hydrogenation reactions (Maccarrone *et al.*, 2012).

2.3 Catalysts for Hydrogenation

2.3.1 Catalysts for Selective Hydrogenation of Acetylenic Compounds, Butadiene and Hexvne

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

Desiderio *et al.* (1975) claimed a patent about selective hydrogenation of vinyl-acetylene. They studied the hydrogenation of a small amount of vinylacetylene in butadiene stream, used 2 packed-bed reactors and packed by 0.05-0.2% palladium on alumina in mixed phase condition (pressure 6-8 atm and temperature 40-60 $^{\circ}$C) and liquid phase condition (pressure 20 atm). They found that the conversion and 1,3-butadiene selectivity of vinylacetylene hydrogenation in mixed phase condition are greater than the vinylacetylene hydrogenation in 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 mixed catalysts which they were obtained by calcinations of bayerites at 960-1200 $^{\circ}$C were 100/0, 80/20, 40/60 and 0/100 (%) θ/α-Al_2O_3 and the reaction study was performed at 50 $^{\circ}$C and atmospheric pressure. They found that the BET surface area and acidity decreased with increasing of α-Al_2O_3 weight percent. While high Pd dispersion and support acidity resulted in high hydrogenation rate, the bimodal pore structure of the mixed phase Al_2O_3 played important role in lowering butane selectivity. Pd supported on 80/20 θ/α-Al_2O_3 had the best performances.

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 use of sol-gel method resulted in only the formation of $NiAl_2O_4$ and the use of solvothermal method gave both $NiAl_2O_4$ and NiO. The addition of Ni atoms was resulted in decreasing of acidity of the nanocrystalline α-Al_2O_3. The

catalytic performance improvement was presumably due to both Pd surface activity modification due to the formation of $NiAl_2O_4$ and a decrease in surface acidity of α-Al_2O_3. The Pd catalysts supported on nanocrystalline α-Al_2O_3 and Ni-modified α-Al_2O_3 showed higher catalytic performances in selective acetylene hydrogenation than the commercial α-Al_2O_3.
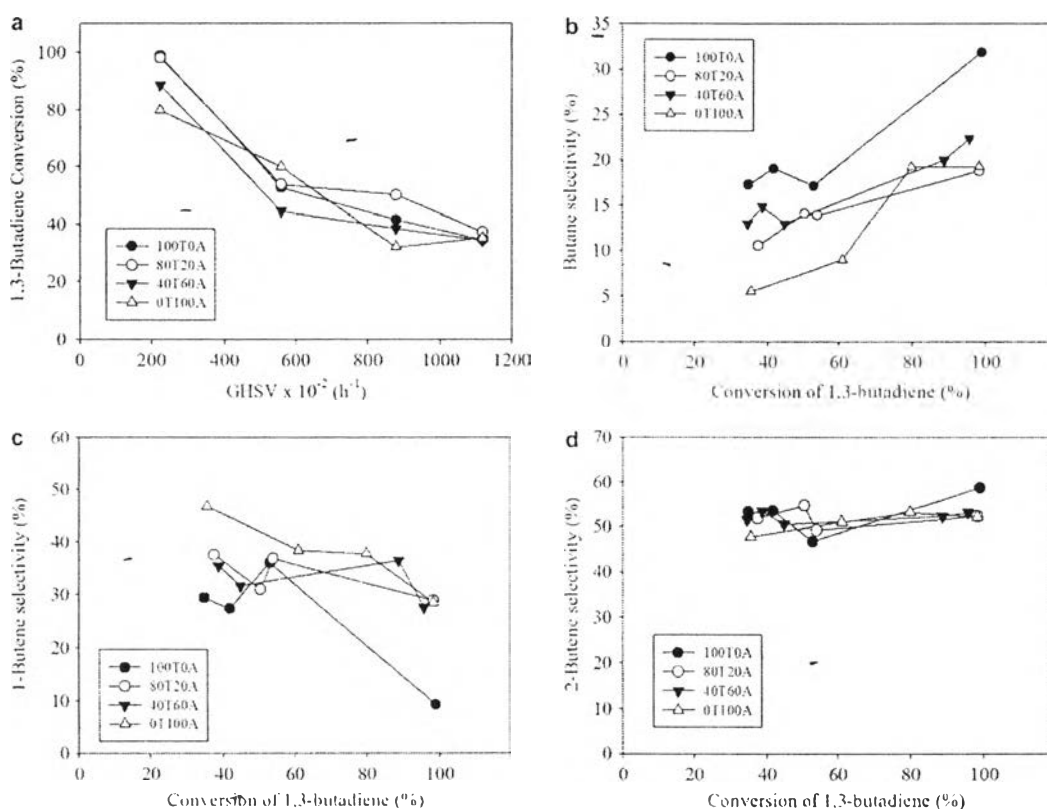

Figure 2.14 The catalytic performances in the gas-phase hydrogenation of 1,3-butadiene (a) 1,3-butadiene conversion (b) butane selectivity (c) 1-butene selecyivity and (d) 2-butene selectivity (Pattamakornsan *et al.*, 2010).

Tew *et al.* (2011) studied the formation and characterization of PdZn alloy of 1-pentyne semihydrogenation catalyst. The formation of PdZn alloy from Pd/ZnO was characterized by combined in situ high-resolution X-ray diffraction (HRXRD) and X-ray absorption spectroscopy (XAS). They found that PdZn alloy formation by reducing Pd/ZnO catalyst started around 100°C and the amount of alloy would be increased with temperature at the consumption of palladium. The activity

of the gas-phase hydrogenation of 1-pentyne reduced with PdZn alloy formation. The PdZn alloy could change the electronic property of palladium and dilute the palladium site at surface which caused to increase the selectivity of pentene and decrease the formation of pentane.
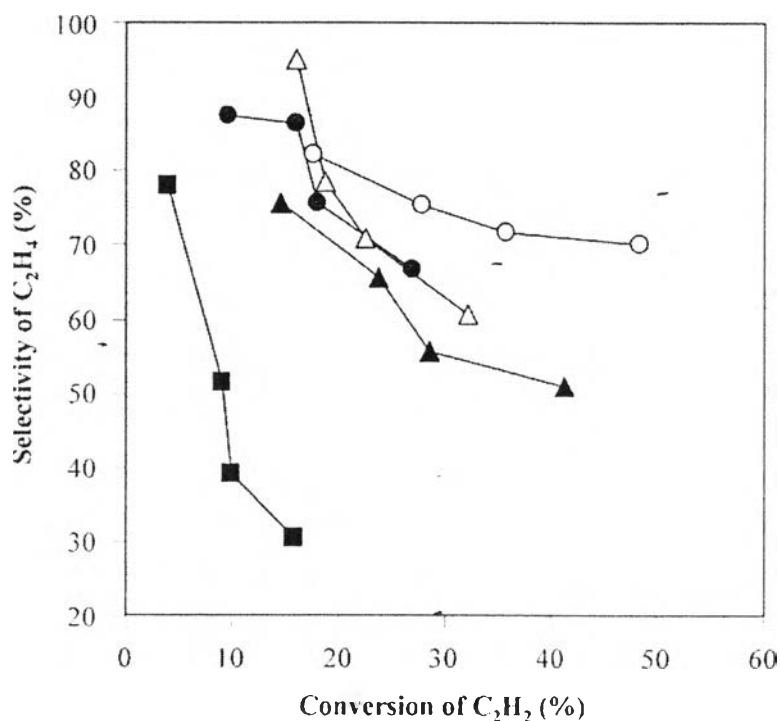

Figure 2.15   Performance of sol-gel and solvothermal made Pd/α-Al$_2$O$_3$. Pd/commercial α-Al$_2$O$_3$ and Pd/Ni-modified α-Al$_2$O$_3$ catalyst in selective acetylene hydrogenation (Wongwaranon *et al.*, 2008).

Huang *et al.* (2007) studied the selective hydrogenation of acetylene in the presence of ethylene at room temperature by using Pd, Ni, Ag, Pd-Ni and Pd-Ag supported on γ-Al$_2$O$_3$ and Na$^+$-β-zeolite as a catalyst. The catalysts were synthesized and assessed by using FTIR batch reactor. They found that Pd-Ag bimetallic catalysts have higher selectivity for acetylene hydrogenation in the presence of ethylene than either Pd or Ag monometallic catalysts. The selectivity of acetylene hydrogenation of Na$^+$-β-zeolite supported catalysts showed higher than their γ-Al$_2$O$_3$ supported counterparts and zeolite supported Pd-Ag bimetallic catalyst

had the highest selectivity of the overall catalysts, whereas Pd-Ni showed similar to the Pd monometallic catalyst.
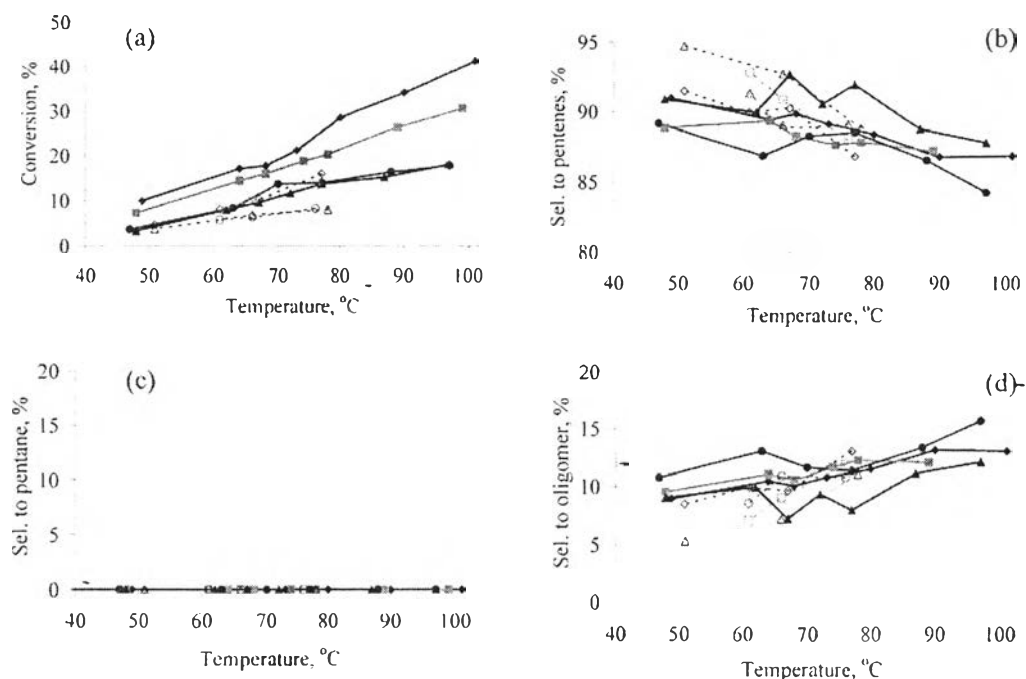

Figure 2.16 (a) Conversion of 1-pentyne over Pd/ZnO reduced at different temperature and corresponding selectivity to (b) pentene, (c) pentane and (d) oligomers (Tew *et al.*, 2011).

Pachulski *et al.* (2011) studied the performance and regeneration of Pd-Ag supported on alumina catalysts for the selective hydrogenation of acetylene. The disadvantages of commercial Pd-Ag/Al_2O_3 catalyst applied in C_2-tail end-selective hydrogenation were relatively short cycle time caused by the formation of green oil and coke deposition. They found that the long-term stability of Pd-Ag/Al_2O_3 catalysts which contained the Ag/Pd-ratio of 0.41 and the lowest concentration of silver was the highest of all with regard to activity and selectivity to ethylene compared with the other Pd-Ag/Al_2O_3 catalysts. This low amount of silver caused a higher dilution of the palladium surface area than the higher amount of silver within the studied catalysts. The number of neighbored palladium surface atoms is decreased by the enrichment of silver on the catalyst surface. Furthermore, the used catalysts could clean completely from the coke deposition by using a

thermal treatment in a steam-air-mixture and a treatment in hydrogen at more than 120 °C.
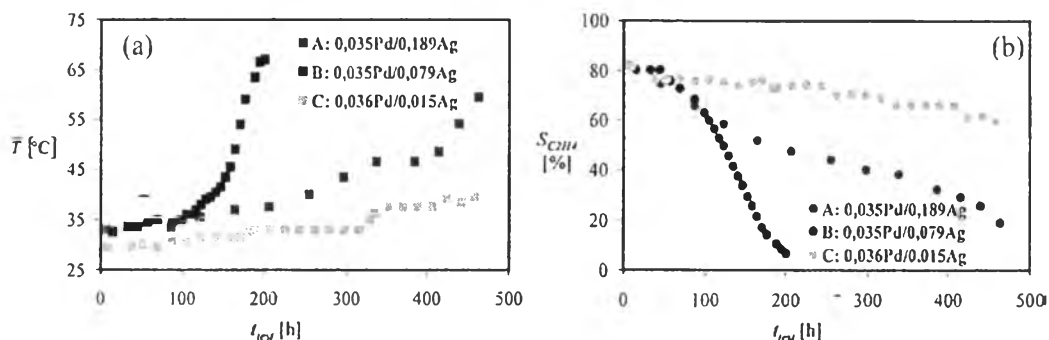

Figure 2.17 (a) Temperature and (b) selectivities to ethylene during 500 h catalytic test (Pachulski *et al.*, 2011).

Sarkany *et al.* (2002) studied the hydrogenation of acetylene in an atmospheric pulse-flow reactor by using low loaded Pd and Pd-Au/SiO$_2$ catalysts. The hydrogenation of acetylene and formation of surface deposits were studied on two series of Pd and Pd-Au/SiO$_2$ catalysts differing in metal particle size. They found that a large excess of hydrogen restrained the formation of carbonaceous and increased the over-hydrogenation of acetylene. The addition of Au to Pd/SiO$_2$ could decrease the carbon coverage and improve the ethene selectivity.

Pattamakomsan *et al.* (2010) studied the gas-phase selective hydrogenation of 1,3-butadiene over Pd and Pd-Sn catalysts supported on mixed phase Θ/α-(MA) and pure α-alumina (AA). The reaction study was carried out in fixed-bed reactor at 30-70°C and atmospheric pressure. They found that butane was formed and 1-butene was isomerized at a high 1,3-butadiene conversion for the monometallic Pd catalysts. On the contrary, the bimetallic Pd-Sn catalysts exhibited 100 % butane selectivity at the high 1,3-butadiene conversion without any loss of 1-butene to butane or 2-butene. The addition of tin played an important role in modifying the electronic properties and the nature of surface sites. Nevertheless, Pd-Sn/AA resulted in a lower Pd dispersion and much lower activity than Pd-Sn/MA in the selective hydrogenation of 1,3-butadiene.
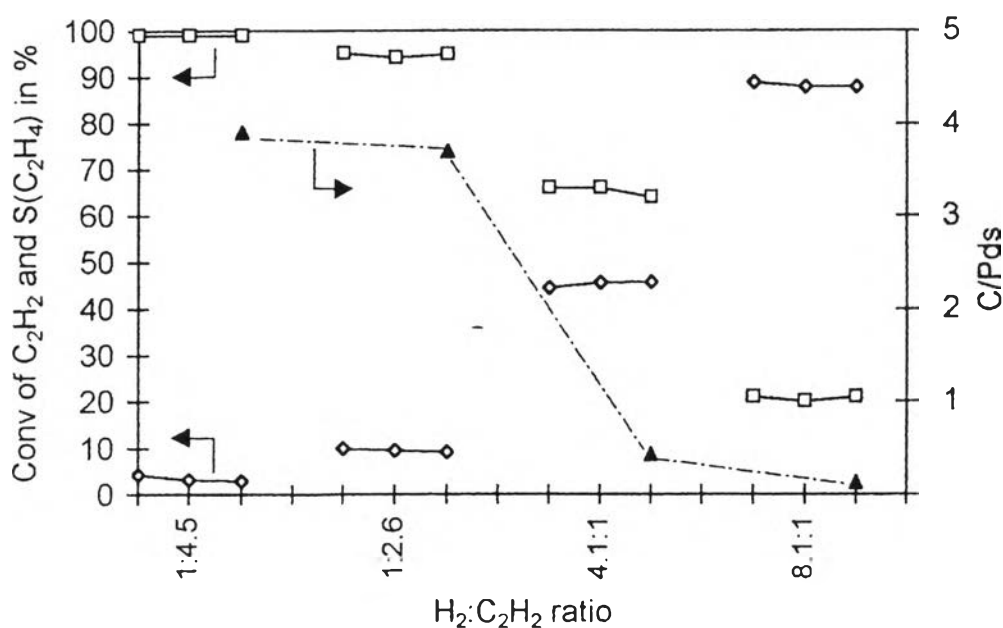
Figure 2.18 Conversion of acetylene, ethane selectivity and amount of deposit in C/Pd_S measured after the third pulse (Sarkany *et al.*, 2002).

Furlong (1994) studied the vapor-phase selective hydrogenation of 1,3-butadiene in the presence of a 10:1 excess of 1-butene over supported bimetallic catalysts contained palladium in plug flow reactor in the temperature range 288-313 K. They found that the activity and selectivity of $Pd-Cu/Al_2O_3$ catalysts were higher than monometallic catalyst. The bimetallic catalysts could increase the selectivity of 1,3-butadiene hydrogenation without saturating or isomerizing the *n*-butenes. Both Pd/Al_2O_3 and $Pd-Cu/Al_2O_3$ catalysts were first order in hydrogen and zero order in butadiene.

Kim *et al.* (2011) studied the performance of Cu and Ag-promoted Pd on alumina catalysts in acetylene hydrogenation. Cu-promoted Pd on alumina catalysts were prepared by selectively adding Cu using a surface redox method, and compared their activity and selectivity with Ag-promoted Pd on alumina catalysts which were prepared by both the surface redox method and conventional impregnation method. They found that the Cu-promoted catalysts prepared by the surface redox method showed higher ethylene activity and selectivity than Ag-promoted catalysts, especially with a small amount of added promoter.
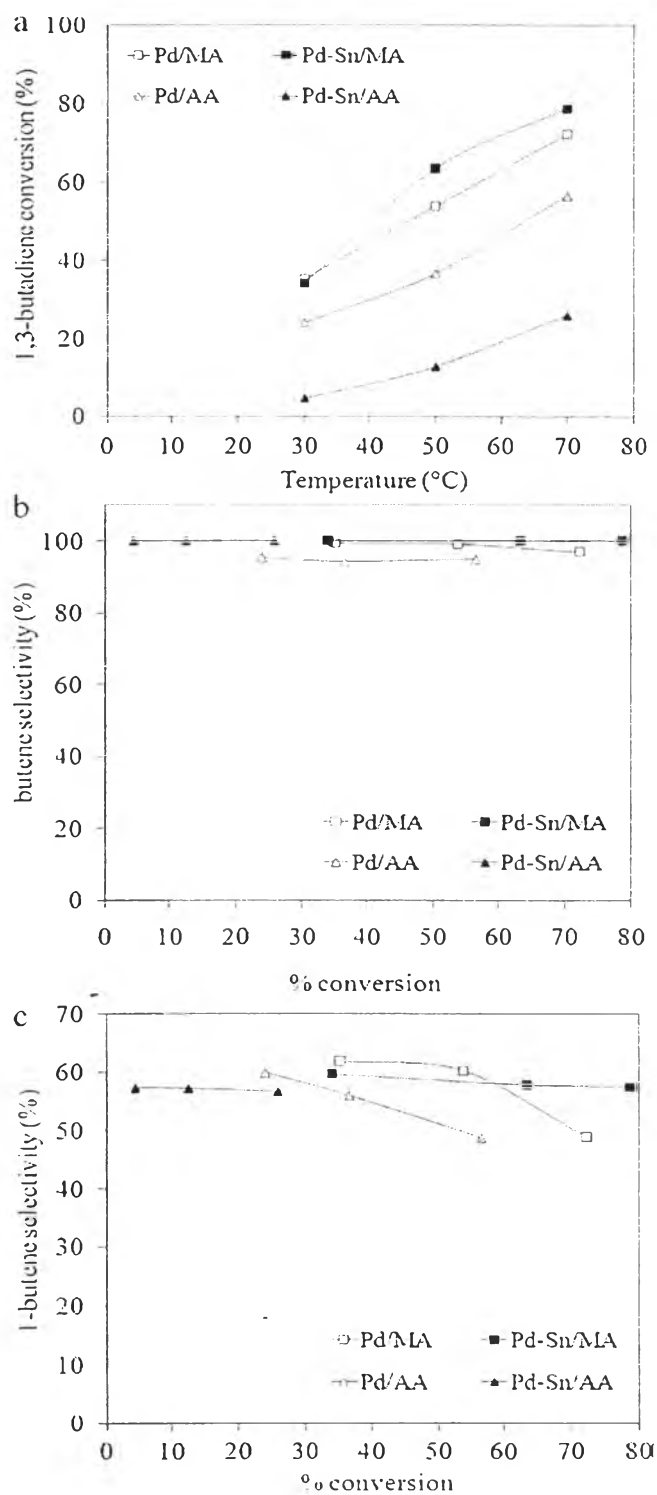
Figure 2.19 Catalytic performances in the selective hydrogenation of 1,3-butadiene (a) 1,3-butadiene conversion, (b) butene selectivity and (c) 1-butene selectivity (Pattamakomsan *et al.*, 2010).
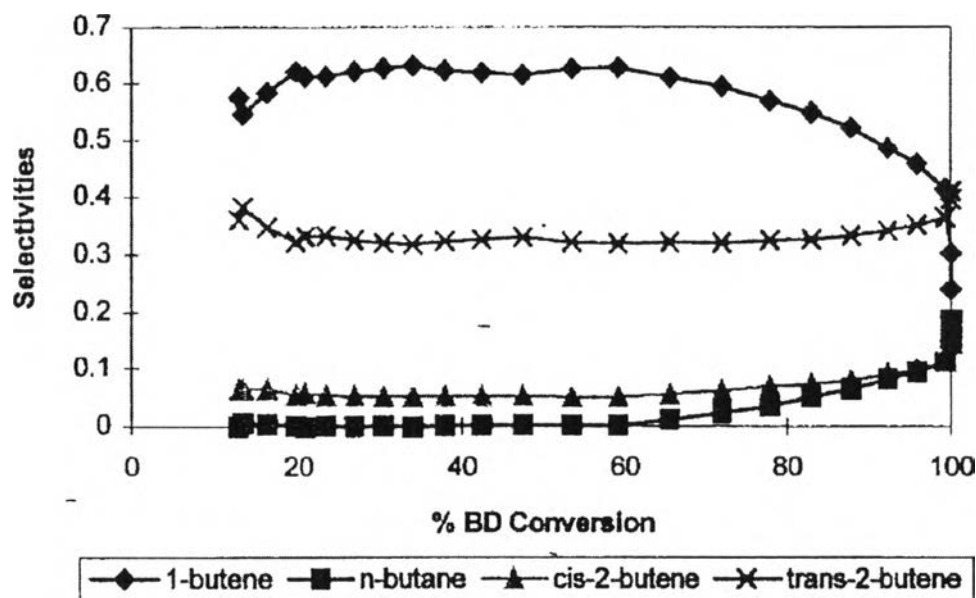
Figure 2.20 Selectivities for *n*-butene and butane formed during butadiene hydrogenation at 288 K and the conversion levels were changed by varying the space velocity between 0.1-1.0 (Furlong *et al.*, 1994).

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 by varying palladium (S:Pd) molar ratios. The catalysts were prepared by impregnation using a toluene solution. They found that the most active catalyst was 1% Pd/SBA-15 which compared to 1% Pd/MSU-γ, 1% Pd/MCM-48 and commercial 1% Pd/Al_2O_3 catalysts. This obtained results could be ascribe to several factors, such as the mesoporous framework effect, differences in the textural porosity and the size of the metal particles or the metal particle dispersion effect on the catalysts.

Crespo-Quesada *et al.* (2011) studied the liquid-phase selective hydrogenation of 1-hexyne by using palladium/carbon nanofiber/sintered metal filter reference catalyst and nitrogen-modified palladium catalyst. The hydrogenation reactions were carried out in a semi-batch stainless steel reactor. They found that the N-modified Pd nanoparticles catalysts were considerably more selective (up to 98.5% at 25% conversion) than a reference catalyst with non-modified Pd nanoparticles on

the same support (88%). Furthermore, the high selectivity was kept up to full conversion, and thus, the over-hydrogenation was restrained due to a site-blocking effect of the N-containing ligands.
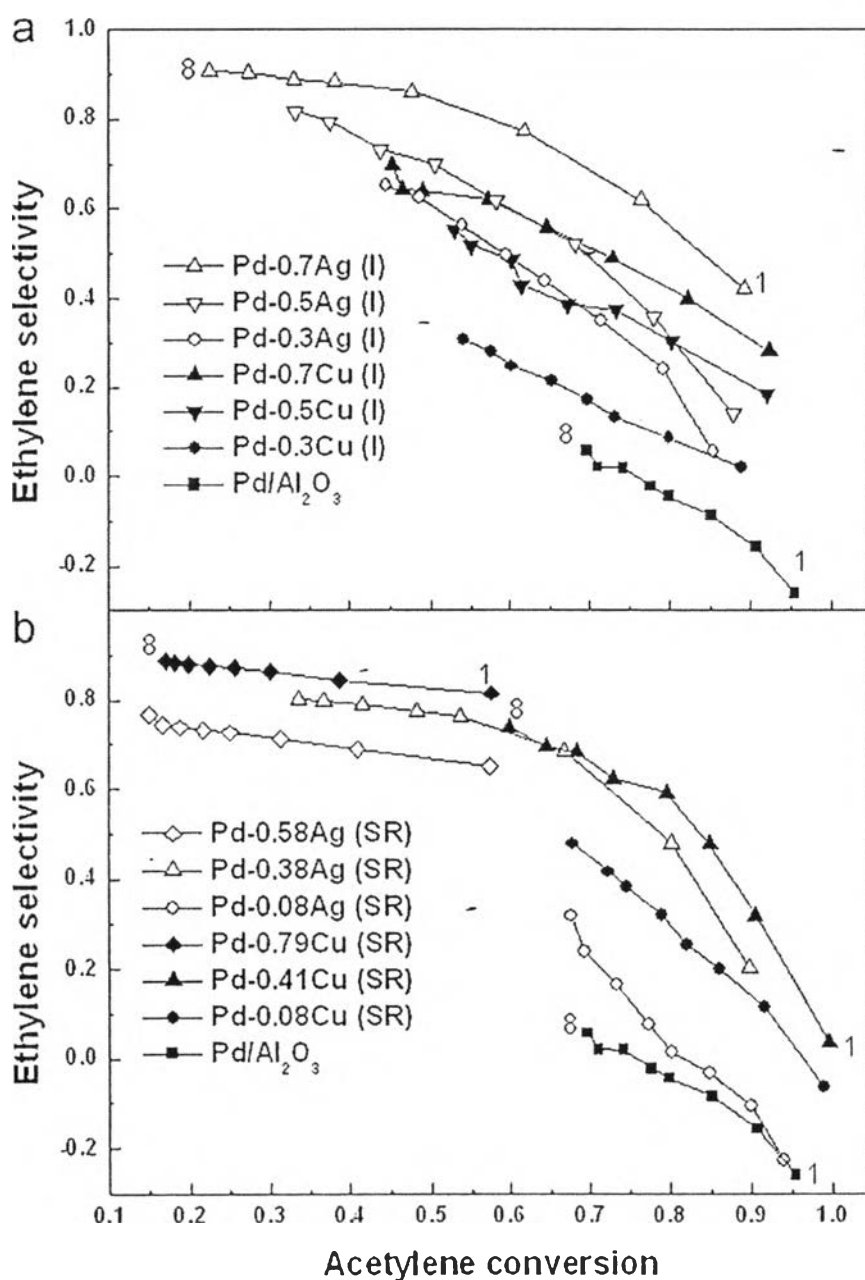

Figure 2.21 Results of acetylene hydrogenation obtained using catalysts containing either Ag or Cu, which was added by (a) impregnation or (b) surface redox (SR) reaction (Kim *et al.*, 2011).
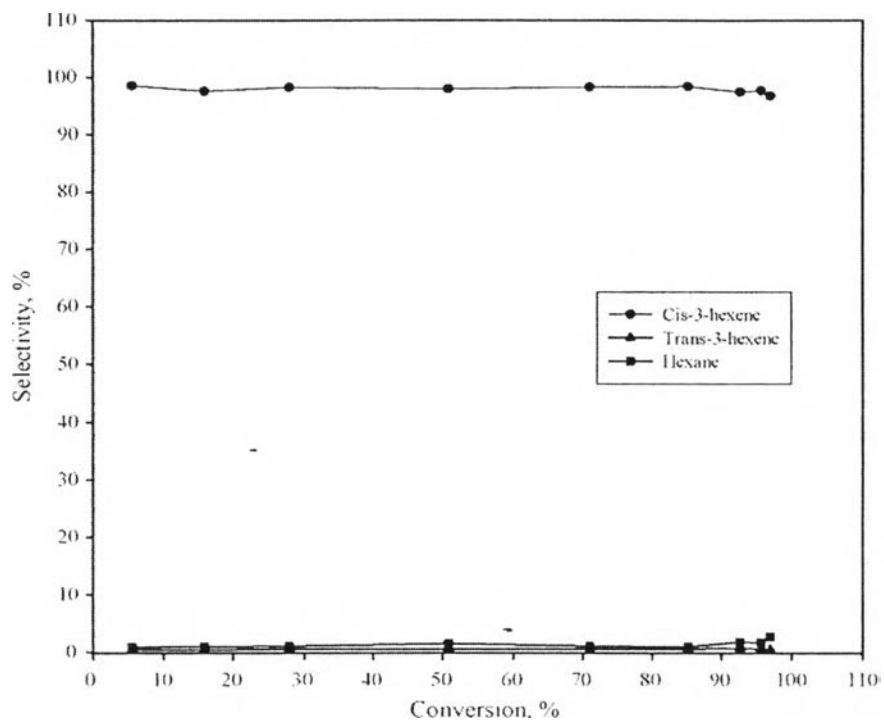
Figure 2.22 *cis*-3-Hexene selectivity as a function of conversion for 3-hexyne hydrogenation over 1% Pd/SBA-15 catalyst at 298 K, P_{H2} = 40 psig and S/Pd = 11,000 (Alvez-Manoli *et al.*, 2010).
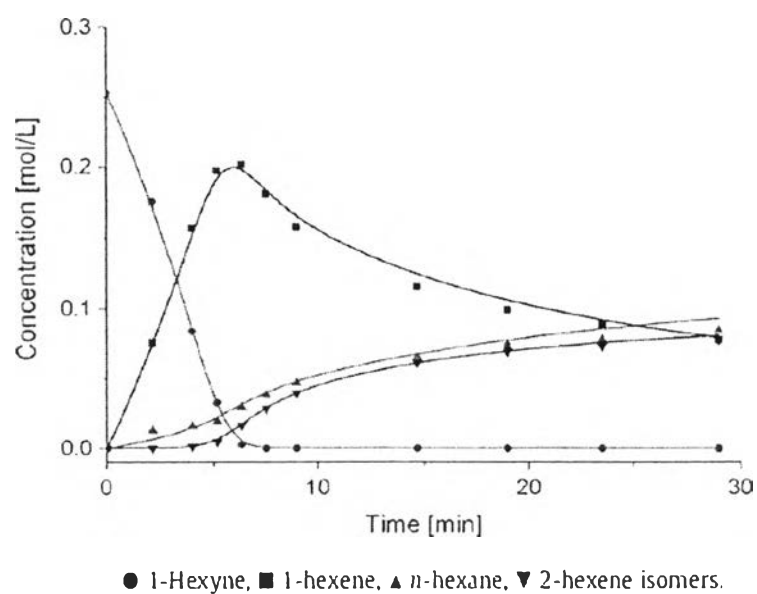

● 1-Hexyne, ■ 1-hexene, ▲ *n*-hexane, ▼ 2-hexene isomers.

Figure 2.23 Experimental points and kinetic curves modeled for the reference catalyst (Crespo-Quesada *et al.*, 2011).
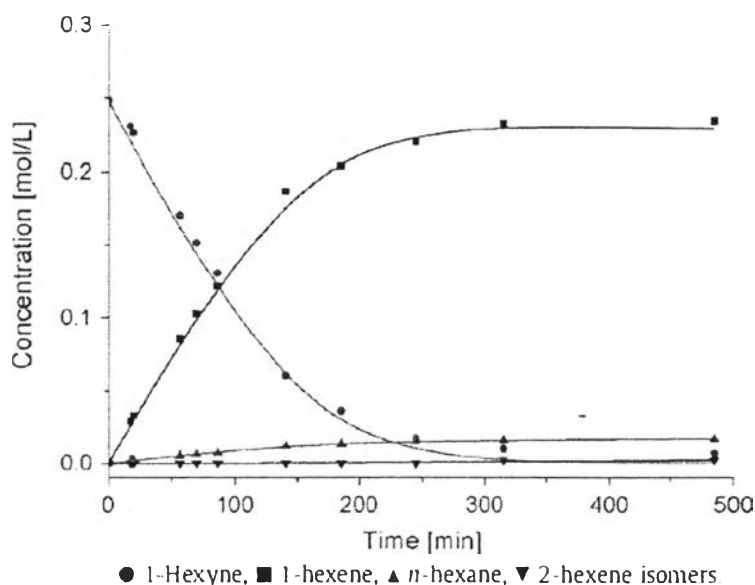
Figure 2.24 Experimental points and kinetic curves modeled for the N-modified Pd catalyst (Crespo-Quesada *et al.*, 2011).

Maccarrone *et al.* (2012) studied the partial hydrogenation of 3-hexyne over low-loaded palladium mono (Pa/A) and bimetallic (PdNi/A and WPd/A) catalysts supported on γ-alumina catalysts with low metal content. The Lindlar commercial catalyst which generally used in these reactions was used for comparative objectives. 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 catalysts and higher than Lindlar catalyst.

Anderson *et al.* (2009) studied the hydrogenation of 1-hexyne and 2-hexyne by using Pd catalyst modified by Bi and Pb. Catalyst behavior was compared with a commercial Lindlar catalyst and Pb-free Pd/CaCO₃. They found that Bi had little effect on the rate of the 1-hexyne hydrogenation. Meanwhile, the rate of subsequent reactions of the 1-hexene formed was suppressed. In this case, Bi was a more effective modifier than Pb. In case of 2-hexyne hydrogenation, Bi was a poor

modifier and failed to suppress the reactions of cis-2-hexene. On the other hand, Pb has a significant impact in terms of suppressing reactions of cis-2-hexene.
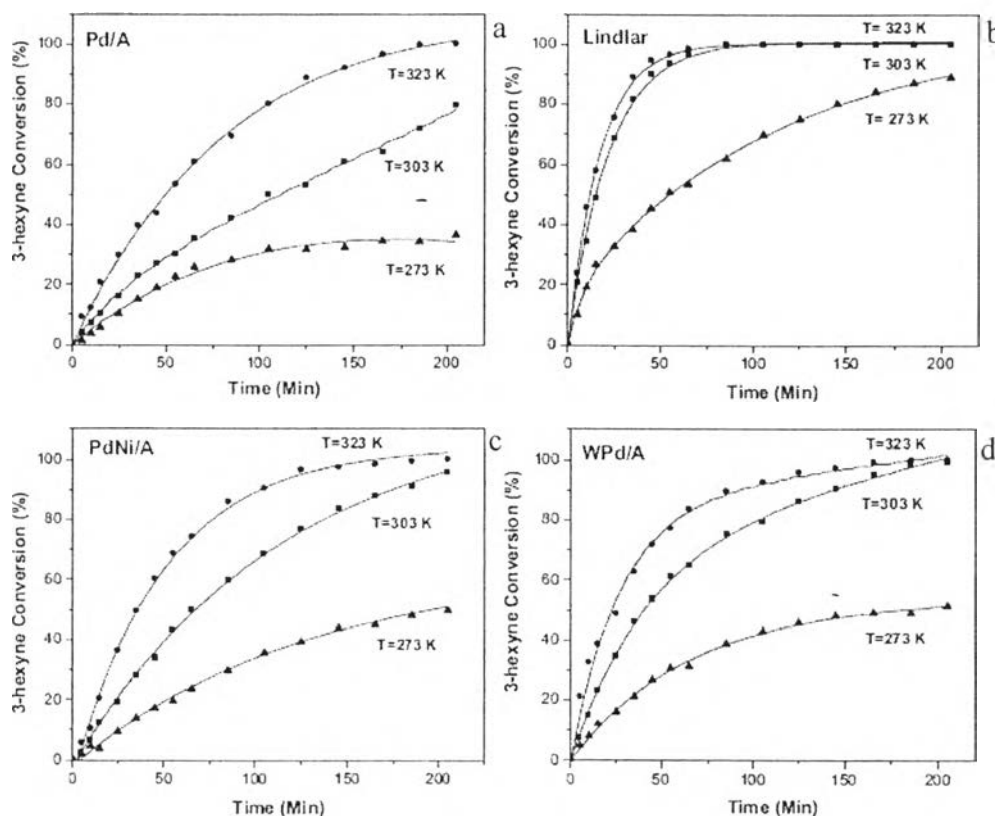

Figure 2.25 3-Hexyne total conversion (%) as a function of time for (a) Pd/A, (b) Lindlar, (c) PdNi/A and (d) WPd/A catalysts, measured at 1.5 bar and different temperatures: T1 = 273 K (▲), T2 = 303 K (■) and T3 = 323 K (●) (Maccarrone et al., 2012).

Lederhos et al. (2011) studied the partial hydrogenation of hept-1-yne by using supported Pd and W catalysts. The mono and bimetallic Pd and W catalysts supported on Y-alumina with low metal content were used. The catalytic reaction tests were carried out in a stainless steel stirred tank batch reactor at 303 K and 150 kPa. XPS, XRD, TPR and hydrogen chemisorption techniques were used for the characterization. They found that monometallic Pd catalyst showed a high selectivity but it was the least active. The bimetallic catalysts were more active than the

classical Lindlar catalyst. The addition of Pd to W on alumina catalyst significantly improved the total conversion and selectivity.
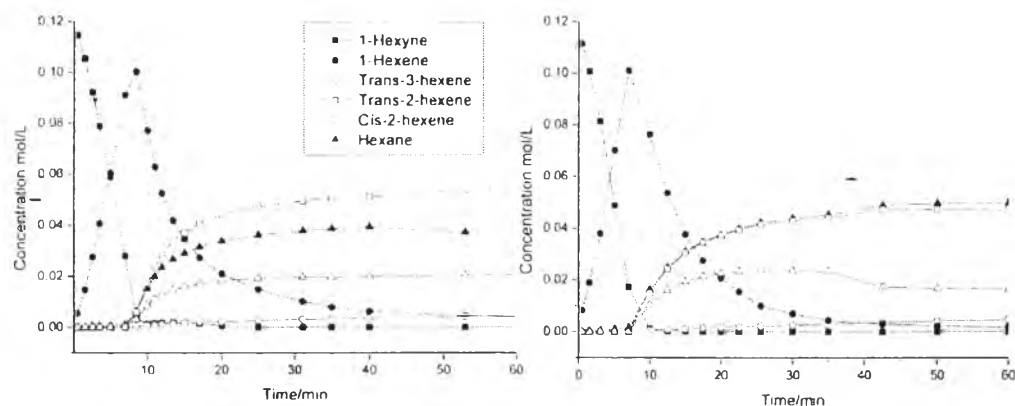

Figure 2.26 Reaction profiles for the hydrogenation of 1-hexyne at 298 K over (left) Lindlar catalysts and (right) 5% $Pd/CaCO_3$ (Anderson *et al.*, 2009).
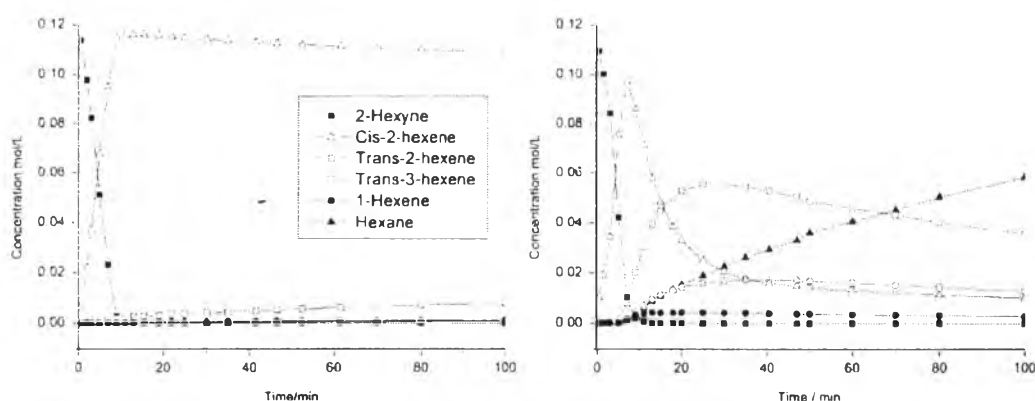

Figure 2.27 Reaction profiles for the hydrogenation of 2-hexyne at 298 K over (left) Lindlar catalysts and (right) 5% $Pd/CaCO_3$ (Anderson *et al.*, 2009).

2.3.2 Mn-Promoted Catalysts for Hydrogenation

Han *et al.* (2004) studied the effect of transition metal (Cr, Mn, Fe, Co, Ni and Cu) on the hydrogenation properties of chloronitrobenzene over Pt/TiO_2 catalysts in ethanol at 303 K and normal pressure. They found that the order of the hydrogenation rate of chloronitrobenzene was $m > p > o$, and the yield of chloroaniline (CAN) was $p > m > o$. The conversion of chloronitrobenzene was

more than 99% and a main product on the hydrogenation of chloronitrobenzene over PtM/TiO$_2$ catalysts was chloroaniline. PtFe/TiO$_2$ catalyst shows the highest selectivity of chloronitrobenzene to chloroaniline. The addition of Fe over Pt/TiO$_2$ on the hydrogenation of p-chloronitrobenzene resulted in increasing of catalytic activity and yield of p-chloronitrobenzene. There were no distinct effect on the catalytic activity and yield of m- chloroaniline for Pt/TiO2 catalyst promoted by Ni, Co and Mn.
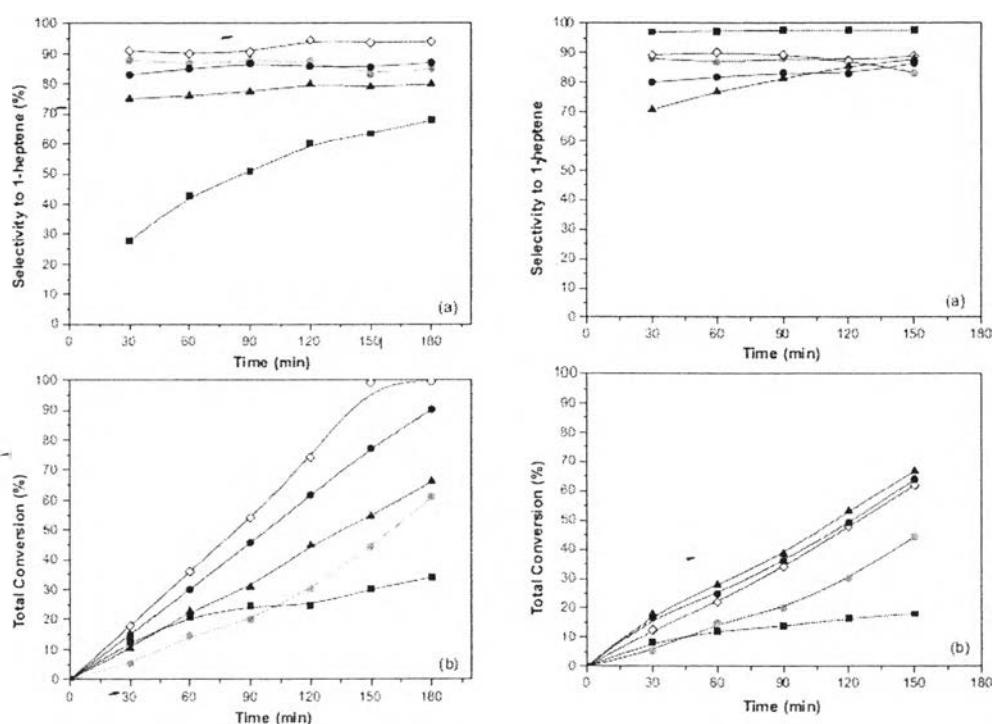

Figure 2.28 Hept-1-yne reaction test (303 K, 150 kPa) results. (a) selectivity to hept-1-ene (%) and (b) total conversion (%) as a function of reaction time over (left) WAl catalysts and (right) PdAl catalysts (Lederhos et $al.$, 2011).

Karavanov et $al.$ (1995) studied the porous membrane catalysts with Pd-M-clusters and less than 1.5% of Pd in porous stainless steel for liquid hydrogenation of dehydrolinalool. Ultra Pd modified with second metal Pb, Mn or Bi was prepared using metal vapour synthesis techniques. They found that the reaction rate over 12 mol/m^{2}h and selectivities up to 96 % in hydrogenation of dehydrolinalool to linalool under atmospheric pressure of H$_2$ were investigated. The

reaction was zero order with respect to the substrate. With decreasing Pd concentration and increase of the second metal concentration resulted in increase of the selectivity. The activity and selectivity of Pd-Mn-catalysts had to depend on Mn concentration. More or less stable selectivities of Pd-Mn-catalysts with Mn concentrations higher than 30 wt % were observed. The catalyst which was higher Mn concentrations could indicate that the active phase of the catalyst has the same composition, but the increase of Mn concentration only blocked some of the active surface.
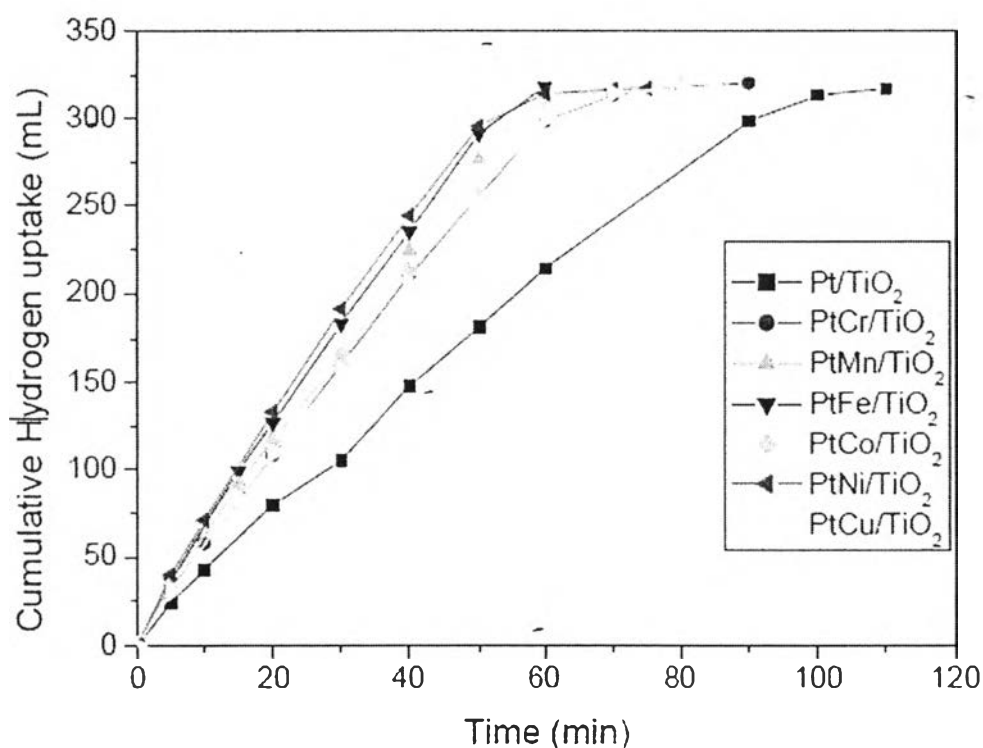

Figure 2.29 Cumulative hydrogen uptake profiles of catalytic hydrogenation of *p*-CNB over PtM/TiO₂ catalysts (Han *et al.*, 2004).

Zhou *et al.* (2011) studied the liquid-phase selective hydrogenation of benzene to cyclohexene on Ru-based catalysts promoted with Mn and Zn. Ru-based catalysts promoted with Mn and Zn were prepared by a co-precipitation method. They found that the catalytic performances of Ru-Mn-Zn catalysts were higher than the catalytic performances of catalysts promoted with Zn or Mn alone. The optimum

Mn/Zn molar ratio was determined to be 0.3. The addition of NaOH could improve the cyclohexene selectivity and yield. The cyclohexene selectivity of 81.1% at a benzene conversion of 60.2% was obtained on the Ru-Mn-Zn-0.3 catalyst with the addition of NaOH.
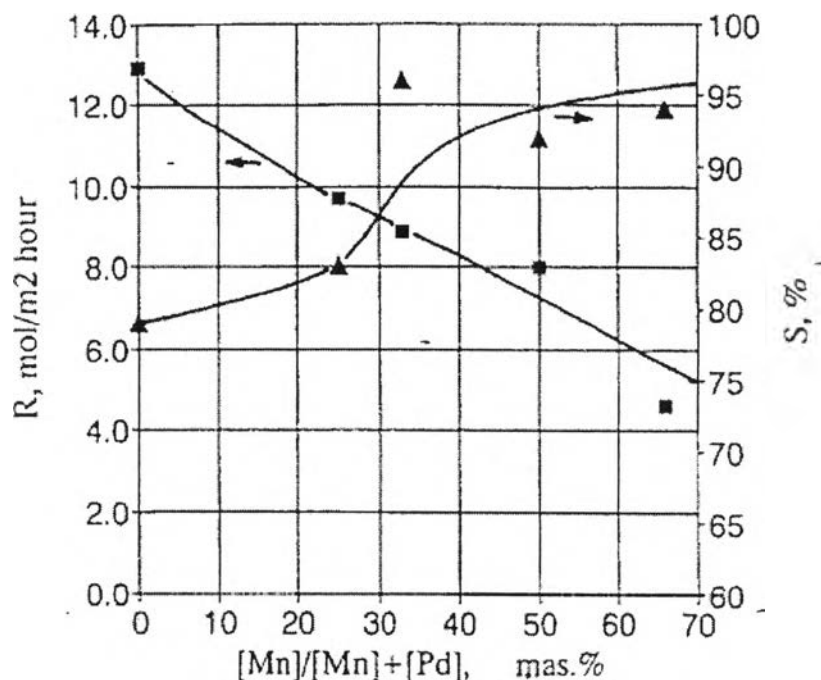

Figure 2.30 Reaction rate and selectivity of Pd-Mn-catalysts in hydrogenation of dehydrolinalool at 150°C (Karavanov *et al.*, 1995).
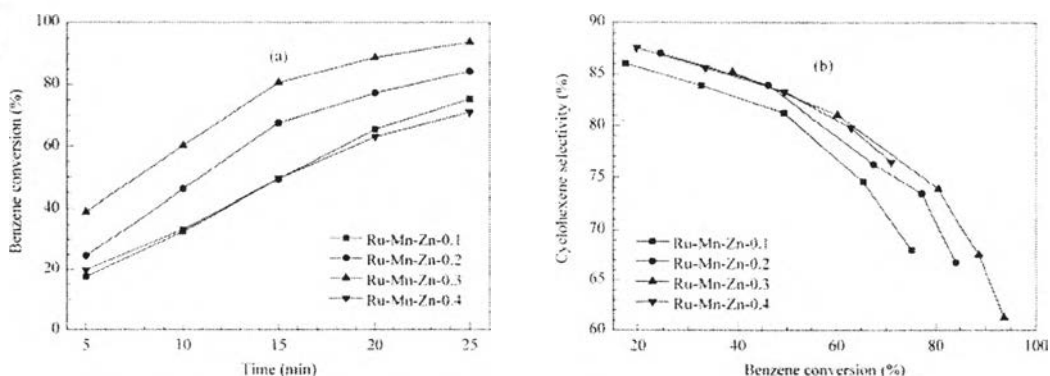

Figure 2.31 Benzene conversion (a) and cyclohexene selectivity (b) on the Ru-Mn-Zn catalysts with different Mn/Zn molar ratios (Zhou *et al.*, 2011).
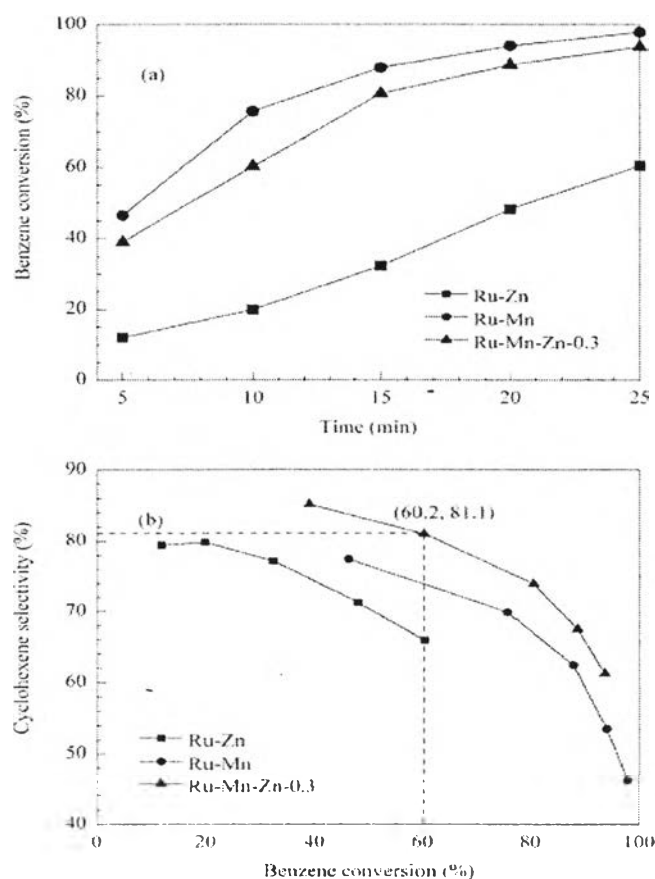
Figure 2.32 Benzene conversion (a) and cyclohexene selectivity (b) on the Ru-Zn, Ru-Mn, and Ru-Mn-Zn-0.3 catalysts (Zhou *et al.*, 2011).

2.4 Catalyst Deactivation -

The catalyst deactivation or the catalyst loss of activity with time-on-stream (Forzatti *et. al.,* 1999) can occur from many problems, such as poisoning, formation of deposits, thermal degradation, mechanical deactivation and leaching.

2.4.1 Coking

Forzatti *et al.* (1999) explained that the side reactions of the catalytic reactions of hydrocarbons could occur on the catalyst surface causing the formation of carbonaceous residues which might deactivate the catalyst either by covering of the active sites and by pore blocking. The difference between coke and carbon was

that carbon was considered the product of CO disproportionation, whereas coke was referred to the material produced by decomposition (cracking) or condensation of hydrocarbons. The coking could be prevented by using an optimal catalyst composition and an appropriate combination of process conditions. An equilibrium was reached between the rate of coke production and the rate of coke removal during the reaction by gasifying agents (e.g. H_2, H_2O and O_2 that remove coke as CH_4, CO and CO_x, respectively) so that steady-state conditions, corresponding to a certain level of coke occurred on the catalyst surface, were finally reached. If the rate of coke production is higher than the rate of coke removal, the catalyst regeneration must be applied.

2.4.2 Poisoning

Forzatti *et al.* (1999) explained that poisoning was the loss of activity owing to the strong chemisorption on the active sites of impurities in the feed stream. The poisons could block the active site or changed the adsorptivity of other species by the electronic effect or changed the chemical nature of the active site which resulted in the formation of a new compound. The difference between poisons and inhibitors was that the interaction between poisons and the active sites was very strong and irreversible, whereas the interaction between inhibitors and the active sites was weak and reversible. Poisoned catalyst could hardly be regenerated, therefore the most suitable way to decrease poisoning was the reduction of the poison content of the feed to acceptable levels. Generally, this was succeeded by appropriate treatments of the feed. For example, catalytic hydrodesulphurization followed by H_2S adsorption or absorption to eliminate S-compounds, methanation for the removal of CO_x from the ammonia synthesis feed and adsorption over suitable beds of solids to remove the trace amounts of poisons.

2.4.3 Leaching

Albers *et al.* (2001) explained that leaching is the loss of precious metal by formation of soluble complex compounds may occur, especially in slurry-phase hydrogenation reactions. The leaching can be prevented by either improving the availability of hydrogen in the liquid reaction medium or optimizing the catalyst side of the process.

2.4.4 Sintering

Forzatti *et al.* (1999) explained that sintering was the loss of active surface by the structural modification of the catalyst. Generally, this was a thermally activated process and a physical in nature. Sintering could occur both in supported metal catalysts and unsupported catalysts. The larger crystallites are more stable than the small crystallites.
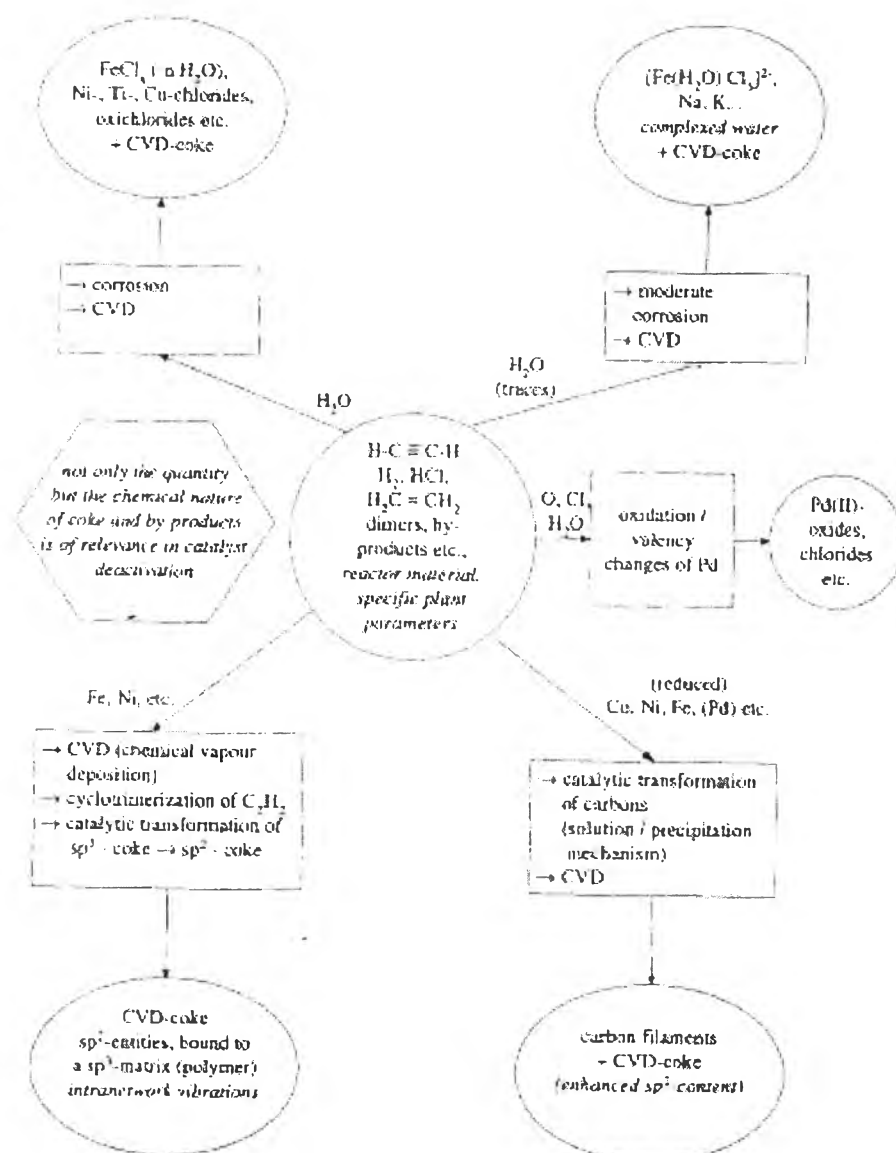

Figure 2.33 Schematic representation of different process observed under various irregular operating conditions during the selective catalytic hydrogenation of acetylene to ethylene in the vinyl chloride process (Albers *et al.*, 2001).