CHAPTER II

LITERATURE REVIEWS

2.1 Hydrogenation

Catalytic hydrogenation refers to the addition of hydrogen to an organic molecules in the presence of catalyst. It is an exothermic reaction and the equilibrium usually lies far toward the hydrogenated product under most operating temperature.

$$A + nH_2 \rightleftharpoons B \qquad H < 0 \qquad (1)$$

As the temperature increases, the equilibrium shifts toward the left and the reverse reaction, dehydrogenation, can itself be a useful process. Industrial hydrogenation requires a mean of limiting the temperature increase arising from the exothermic reaction. A higher temperature usually has a favorable effect on reaction rate, but may affect selectivity and operating conditions.

Hydrogenation is influenced by a number of factors, including catalyst, solvent, substrate purity and operating conditions. Temperature, pressure, agitation and catalyst loading can each influence both the rate and the selectivity of hydrogenation. In general, as temperature, pressure, agitation and catalyst loading increase, the rate of hydrogenation increase until a limit is reached.

2.2 Hydrogenation Catalyst

Hydrogenation can be carried out in both the liquid and the gas phases, but liquid phase reaction are much more common. Hydrogenation catalysts are of two types, heterogeneous and homogeneous. *Heterogeneous catalysts* are solids that form a distinct phase in the gas or liquid environment. *Homogeneous catalysts* dissolve in the liquid medium, forming a single phase.

Homogeneous catalyst are used infrequently in industry. They are difficult to seperate from the reaction media and are not employed if a suitable heterogeneous catalysts is available. Heterogeneous catalysts can be devided into two types, those used in fixed-bed processing, in which the catalyst is stationary and the reactants pass over it, and those used in fluidized-bed or slurry processing. The former have relatively large particle size of 0.79-6.35 mm., in various forms. Slurry or fluidize-bed catalysts are fine powders that can be suspended readily in liquid or gas.

Many metals and metal oxides have general hydrogenation activity. Nickel, copper, cobalt, chromium, zinc, iron and the platinum group (platinum, palladium, rhodium, ruthenium) are among the elements frequently found in commercial hydrogenation catalysts. Combinations of these or other elements are sometimes used to confer additional activity, selectivity, stability, or life.

Palladium, platinum, rhodium, and rhutinium make exceptionally active hydrogenation catalysts and are frequently used when equipment or stability limitations permit operating only under mild conditions. They can effectively reduce most functional groups, usually under more vigorous conditions than the platinum group. Copper chromite is used mainly to reduce ester to alcohol. Cobalt or iron, in the presence of ammonia, is effective for the reduction of nitriles to primary amines.

2.3 Hydrogenation of Benzene

Hydrogenation of benzene had long been known as one of the most important catalytic reactions in the industry. Its product, cyclohexane is used almost exclusively as a precursor for the production of cyclohexanol and cyclohexanone; these chemicals in turn are predominantly used as precursors of nylon 6 and nylon 66.

Benzene, C_6H_6 is usually described as a clear, colorless, volatile, flammable liquid, aromatic in nature, possessing a characteristic odor.

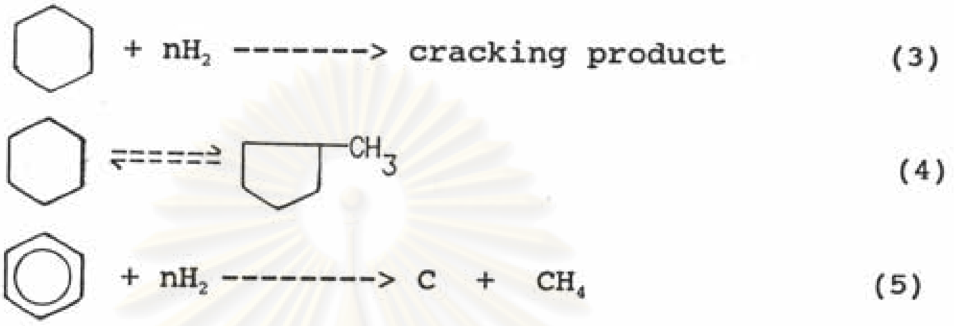
The catalytic hydrogenation of benzene to cyclohexane is a strongly exothermic reaction. It is an irreversible reaction at lower temperature and high hydrogen partial pressure. Moyes and Wells (1973) said that the reaction is generally of approximately first order in hydrogen and approximately zero order or slightly negative order to hydrocarbon. The reaction is written as:

$$C_6H_6 \quad + \quad 3H_2 \quad \text{--------->} \quad C_6H_{12} \qquad (2)$$

$$H \ = -51.2 \text{ Kcal/mole at } 200^{\circ}\text{C}$$

The reaction is therefore favored by a low temperature and a higher pressure. The hydrogenation proceeds cleanly to cyclohexane unless elevated temperature are employed, then cracking and rearrangement into a variety of products occurs (Emmett, 1957).

The various reactions that can occur in the presence of benzene and hydrogenation under vigorous conditions are as follows:



Reaction (3) is of little importance up to temperatures of about 250°C; it can be produced either by a hydrogenolysis-type reaction catalyzed by metal of group VIII, or by a hydrocracking-type reaction catalyzed by bifuntionsl catalyst of a hydrogenating metal deposited on an acid support (alumina or silica-alumina). This hydrocracking can be avoided by choosing a non-acid support.

Reaction (4) is thermodynamically favored by a rise in temperature; it is catalyzed by acidity of the catalyst or of the support.

Reaction (5) occurs particularly in vapor phase. Catalyzed by metal of group VIII, it is relatively enhanced by a rise in temperature and a reduction in pressure.

The catalytic hydrogenation of benzene can be carried out either in the mixed liquid-vapor phase or completely in the vapor phase and the catalyst which can be used for this reaction comprises the group VIII metal such as platinum, palladium, ruthenium and nickel or active metal supported on the high-area oxide support such as Al_2O_3, SiO_3. Commercially, Raney nickel is also used. The temperature and pressure of the reaction depended on the catalyst.

Amano and Parravano (1959) studied the vapor phase hydrogenation of benzene over ruthenium, rhodium, palladium and platinum catalysts supported on aluminuum at one atmosphere hydrogen pressure and temperature from 25 to 225°C, they found the reaction to be essentially first order with respect to hydrogen and zero order with respect to benzene. This result agreed with the study of Bizhanov, et al. (1984) which was conducted at 100-200°C and using the same catalysts. They also found the order of catalytic activity to be Rh > Ru > Pt > Pd.

Vannice and Neikam (1971) hydrogenated benzene at 150°C, 1 atm. H_2, and mole ratio H_2/C_6H_6= 20 in a steady -state flow reactor with a $Pd-Al_2O_3$ catalyst and found that the reaction was zero order in the benzene concentration.

Further studies of benzene hydrogenation was reported by Shinghal, et al.(1978), they investigated the kinetics of this reaction in the presence of Ni/Al_2O_3 catalysts, they found that the rate was zero order in C_6H_6 and ~2.3 order in H_2 and the activity energy was ~ 4.12 kcal/mol at 150-200°C.

Kamarewsky and Miller (1959) found that cyclohexane could be produced from benzene and hydrogen at 475°C and 115 atm over vanadium oxide. The catalyst was inactive for this reaction at 400°C and atmospheric pressure. They were unsuccesful in attemps to hydrogenate benzene over chromium oxide both at atmospheric and super atmospheric pressures.

Phillips Petroleum Co. (1962) also prepared pure cyclohexane by this reaction in which n-hexane is used as a heat absorbant and azeotrope component. A mixture of 1 part benzene, 5.7 parts n-hexane and 7 parts H was fed into a catalyst bed at 232°C and pressure of 432 psi. The crude product stream was cooled, adjusted to a ratio 70:1 n-hexane to benzene, and fractionated in a column operating at 121°C and 60 psi., n-hexanebenzene was remove for recycle from the top of column and pure cyclohexane from the bottom.

A new process for the production of high purity cyclohexane also conducted by Dufan, et al. (1964). They prepared cyclohexane containing < 100 ppm of benzene by the liquid phase hydrogenation of benzene over Raney nickel in suspension at 200°C and > 3 atm partial pressure of H (about 40 atm total pressure). Under these conditions the equilibrium conversion is > 99.99 % and 51.2 kcal/mole are produced. Temperature control is obtained by cooling and recirculation of a portion of reaction mixture, and the last traces of benzene are removed by passing the cyclohexane product as vapor through a fixed catalyst bed with additional H. The final product is normally 99.97 % pure by weight.

Benzene and conjugated alkadienes were hydrogenated to cyclohexane and alkanes over Sn oxides -Pt-Co-Cl catalysts which were also employed in the hydrocracking of heavy hydrocarbons to C_{1-6} alkanes by Pollitzer and

Hayes (1977), the reaction condition were < 500°F, 400-5000 psig and LSHV 0.1-10.0.

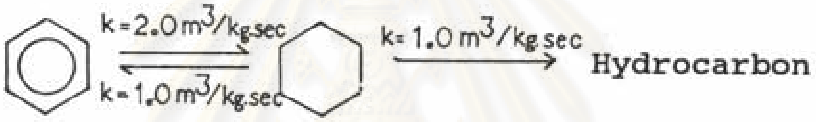
The effect of temperature on vapor phase hydrogenation of benzene to cyclohexane over a Ni-Cr catalyst at 20 atm has been investigated by Proskunin, et al. (1972), they found that the degree of conversion was maximum at 200°C with a space velocity of 1.8 hr^{-1}. They also found that above 200°C , decomposition product were adsorbed on the catalyst surface, thus decreasing its activity.

Later, studies of benzene hydrogenation have been made with iron catalyst. Badillia-Ohlbaum, et al. (1977) found that hydrogenation of benzene over a singly iron catalyst at 130-190°C gave only cyclohexane and cracking product were also found in very a low concentration at temperature above 170°C. One mol of adsorbed benzene simultanouesly reacts with 3 mols of dissociatively chemisorbed H as the rate-controlling step. They also found that a change in the mechanism occurs at above 180°C.

Aizawa and Kuroda (1978) also prepared cycloolefins by partial hydrogenation of aromatics hydrocarbon in the presence of Ru-containing catalyst and phasphates. Thus, a mixture of 0.3g 5% Ru/Al_2O_3, 0.2g of $Mg(P_3O)_4 8H_2O$, 3g of H_2O, 3g benzene and 10 Kg/cm^2 H was autoclaved at 70°C for 4 hr to give 2.1% cyclohexane with 29.9% conversion of benzene and 7.0% selectivity for cyclohexane.

Further work was studied by Franco and Phillips (1980). Gas phase hydrogenation of benzene over nickel-kieselguhr catalyst was studied in the differential flow microreactor at 120 to 195°C benzene partial pressure from 22.66 to 280 Pa, H pressure from 72.39 to 122.79 kPa and cyclohexane partial pressure from 5.33 to 40 Pa. They found that cyclohexane was the only product of the reaction. They observed the maximum in the hydrogenation rate at 185°C.

Reaction network for hydrogenation of benzene proposed by Sapre and Gates (1981) was carried out in a batch reactor at 75 atm and 325°C in the presence of sulfided $CoO-MoO_3/Al_2O_3$. Cyclohexane was the primary product observed. The reaction network is shown below.



(6)

and the reaction is approximated as first order in the organic reactant.

Bogza, et al. (1984) also successfully hydrogenated benzene over Ni at 165-260°C at 8-10 atm. The $H-C_6H_6$ molar ratio was 3.2:10.

Studies of benzene hydrogenation have been made with promoted catalysts. Tanida (Emmett, 1957) found that molybdenum and tungsten were good promoters for nickel catalyst. Corson and Ipatieff (Emmett, 1957) found that small amounts of cobalt and nickel greatly increase the efficiency of copper catalysts in benzene reduction.

Orito and Kowachi (Emmett, 1957) investigated the reaction of hydrogen with benzene in ethanol at 160°C over a nickel-chromium-kieselguhr (1:0.1:1) catalyst. They found that the chromium exerted a promotive action only when it was added into nickel by coprecipitation .

Catalyst prepared by mechanical mixing gave no evidence of promotion.

Zhanabaev, et al. (1982) found that a conversion of C_6H_6 and yield of cyclohexane was achieved in the liquid-phase catalytic hydrogenation at H pressure 7-8 MPa, 150-160°C and C_6H_6 space velocity 0.6-0.9 hr^{-1}. These authors found that a Raney Ni catalyst containing 2% Fe and 3% Nb as promotors was approximated twice as active and stable as a similar catalyst containing 2% Fe under similar conditions.

Sokol'skii, et al. (1982) studied the hydrogenation of benzene using Raney Ni catalyst promoted with Mo or W at 160°C and 8 MPa. The reaction gave high-purity cyclohexane with 100 % conversion and apparent activation energy 6.5-7 kcal/mol.

The hydrogenation of benzene may occure in the presence of a bifuntional catalyst, Nasution (1984) succesfully hydrogenated benzene to cyclohexane over Ni-W/ Al_2O_3 and Ni-Mo/Al_2O_3 at 270-300°C, 10-60 kg/cm^3 and 4-14:1 (molar) H-hydrocarbon and also succesfully used Co-Mo/ Al_2O_3 catalyst at 320-370°C and 10-60 kg/cm^3.

In practice, the selection of catalyst determined from its high activity at low temperature and give the best selectivity. Table 2.1 shows the ability of various catalysts in the hydrogenation of benzene.

Table 2.1 The ability of benzene hydrogenation catalysts

forms	activity
film	W>Pt>Ni>Fe>Pd
Al_2O_3 supported at 47 °C	Rh>Ru>Pt
SiO_2 sopported at 100 °C	Pt>Rh>Ru>Pd>Co>Ni>Fe
others supported	Pt>Ni>Pd

In general, the activity of nickel catalysts toward hydrogenation of benzene is inferior to that of platinum group. However, in industral practice, commercial operations employ a nickel catalyst (gas phase hydrogenation) and fixed-bed Raney nickel (liquid phase hydrogenation) being particularly suitable, as it is superior cheaper. The pressure can be from 100-1000 psig, an average of 700-800 psig being typical. The temperature is 200 = 30°C, and liquid space velocity is approximately 3. The feed composition is approximately 20 % benzene and 80 % cyclohexane. The heat being dissipated both by boil-off of cyclohexane and by specific heat of the liquids. The cyclohexane that boils off is then recyclied in part as a component of feed stream, and the remainder is withdrawn as a product. The reaction can be carried out both in fixed bed or as a slurry-type operation.

2.4 Deactivation of Catalyst

Most catalysts used in heterogeneous catalytic processes are subject to decrease in the initial activity over a period of time. The time required for the activity of a catalyst to fall to an undesirable level varies with the severity of the process conditions and with the type of the reaction being catalysted. The reason why this happens is often very complicated but usually due to four basic mechanisms: (1) sintering or thermal degradation (2) fouling or coking (3) poisoning and (4) loss of catalyst material through formation and escape of vapors. These causes of deactivation of catalyst may occur singly or in combination, but the overall result is to remove active site from the catalytic surface.

2.4.1 Deactivation by Sintering

Sintering or thermal degradation is a physical process associated with the loss of catalyst area due to crystal growth in the catalyst phase, or with the loss of catalyst support areas due to support collaspe which occurs when the catalyst is operated above the normal temperature range. Such temperature rises may occur through out the catalyst or may be localized at individual areas where the reaction occurs. Two different kinds of sintering may be distinguished depending on the type of catalyst employed. If the catalyst is a normal high area support type material, operation at high temperature will cause a loss of specific surface area with associated changes in the pore structure. The second type of catalyst is an active metal supported on a high area oxide support. Here sintering can occur not only by reduction of the support area but by a `coalescence' or loss of dispersion of metal crystallites. These loss of area cause a sharp drop in activity. Sintering can be avioded by working at an operating temperature below the normal range of temperature.

2.4.2 Deactivation by Fouling

Fouling is a process of catalyst deactivation that may be either physical or chemical in nature. In general, much larger amounts of material are responsible for deactivation in the fouling process than in poisoning. Fouling is a physical deposition of species from the fluid phase on to the catalyst surface. This result in blockage of reaction sites or pore with consequent loss of active catalyst areas, and in extreme case, it may even lead to blockage of the interparticle void spaces and completed blockage of the reactor. The most fouling process is that of carboneceous deposits or `coke' that forms on most catalysts used in the processing of petroleum fractions or the other organic chemical feedstocks. The formation of this carboneceous or coke deposits (containing, in addition of carbon, significant amounts of hydrogen plus traces of oxygen, sulfur, and nitrogen) during the processing of organic base chemical feedstocks in this case originates from the reaction occuring and it is not an impurity. Because of this intrinsic association with the main chemical reactions, fouling by coke cannot be eliminated by purification of the feed or use of a guard catalyst; if reaction occurs, coke deposition must also neccessarily occurs according to the overall chemistry of the process. However, coke formation can be minimized by appropriate choice of reactor and operating conditions, and in some case by modification of catalyst.

In general, coke can originate from the reactant or product by reaction (7) or (8). Reaction (7) is called parallel fouling while (8) is called series fouling or consecutive fouling. Fouling may also occur by a combination of reaction (7) and (8). The extent of coke formation will depend on the order of the reaction with respect to the formation of the desired product R and the coke, and on the magnitudes of the temperature coefficients for each reaction. Coke deposition will increase when the reaction rate is greatest.

$$A \longrightarrow \left\{ \begin{array}{l} \longrightarrow R \text{ (main reaction)} \\ \longrightarrow \text{Coke (side reaction)} \end{array} \right. \tag{7}$$

$$A \longrightarrow R \longrightarrow \text{Coke} \tag{8}$$

Another class of fouling reactions is that of metal sulfide deposition rising from the organometallic constituents of petroleum which react with sulfur containing molecules and deposit within the pores of catalyst during hydrotreating operations. In this case, the metal site of the organometallic compounds will be adsorbed on the catalyst surface and the other site, organic site, will be polymerized. Then fouling will occur.

2.4.3 Deactivation by Poisoning

The term poisoning will be used solely to describe catalyst deactivation due to small amounts of material, specifically to a specific catalyst and associated with the adsorption of the poison on the active sites of the catalyst. Poison is often associated with contaminants such as sulfur, nitrogen, oxygen compounds in the feed stream of petroleum fraction which is then termed impurity poisoning. Though this is the most well documented and the best identified of poisoning processes, it is important to recognize that other forms of poisoning may occur. These include poisoning by product of the desired and undesired reaction which may be preferentially adsorbed on the active sites of the catalyst. Thus retarding the adsorption of reactant. Another poisoning is deactivation by metals which are the impurities in the petroleum feedstocks. Trace of metal impurities can permanently deposit on the active sites of the catalyst surface and cause a loss of catalytic activity. The deposition of metal impurities is considered to have a long term deactivation effect.

Catalyst poisons can be classified in various ways, such as by degree of affinity for the surface, a temporary and permanent, or as selective and non-selective. In particular, distinction can be made between temporary and permanent poison, appoint which rests upon the degree of reversibility of chemisorption on the surface, and inhibitors of reaction rate which are either reactants or products of the main reaction being carried out. The description of a poison as selective or non-selective is related to the nature of the surface and the degree of the interaction of the poison with the surface. A nonselective case is the chemisorption of poison on the surface which removes active sites in an uniform manner, such net activity of the surface is the direct function of the amount of the poison chemisorped. In essence, every active sites looks like every other active sites to the poison molecule. Conversely, in selective poisoning there will be some distribution of properties of the active sites, such as acid strength, which can be the result of any member of factors but which results in non-uniform deactivation of the surface. Often these will appear as exponential or hypobolic relationships between the net activity of the surface and the amount of poison chemisorped.

Most poisoning processes are effectively irreversible, so the catalyst has to be discarded ultimately, but there is an important class of poisons that are reversible in action. Example include the poisoning of the reforming catalyst by sulfur, the poisoning of nickel hydrogenation catalyst by oxygen and by water vapors, the poisoning of cracking catalyst by nitrogen. Therefore it is always possible to remove impurity poisons from the feed stream before using it in the process by hydrotreating reaction. Such as hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation is used for removing sulfur, nitrogen, oxygen impurity from the petroleum feedstocks, respectively.

2.4.4 Deactivation by the Loss of Catalytic Metal

The loss of catalytic metal through the formation of compounds such as metal carbonyls, oxides, sulfides and halides in environments containing CO, NO, O_2, H_2S and halogens is the fourth mechanism of catalyst decay. In each case the catalyst life will depend on operating variables.

2.4.5 The Theory of Catalyst Poisoning

Earlier work on the poisoning of metallic catalysts was brought together by Maxted (1951). In this he proposed a theory of catalyst based on the electron structural properties of the poisoning in the gas phase and the solid metal catalyst. The concept employed is that essentially the poison is adsorbed on the active metal sites to form a chemisorped complex. Limitation to chemically bounded systems implies a specificity and also that a low concentration of poison may have a very marked deactivating effect. Metallic catalysts susceptible to poisoning are confined mainly to metals of group VIII of the periodic table and the closely related metal of group IB (Cu, Ag, Au). These are listed in table 2.2 ;most of them are employed for hydrogenation and reforming reaction, and much of the earlier work on poisoning were performed on this type of catalyst.

Table 2.2 Catalytic metals most susceptible to poisoning

Fe	Co	Ni	Cu
Ru	Rh	Pd	Ag
Os	Ir	Pt	Au

The principle poisons that are effective in deactivating these metal catalysts belong to the following groups:

(a) Molecules containing elements of the periodic table Group VB and VIB i.e. N, P, As, Sb, and O, S, Se, Te.

(b) Compounds of a large number of catalytically toxics metal.

(c) Molecules containing multiple bonds, such as CO, cyanogen compounds, and strongly adsorbed organic molecules.

The toxicity of compounds of group VB and VIB was attributed by Maxted to the presence of unshared electron pairs which facilitated the chemisorption process. Thus compounds such as H_2S, PH_3, and organic sulfided function are poison whereas compounds with no lone electron pair are non-toxic.

2.5 Deactivation of Catalyst in Hydrogenation of Benzene

Deactivation of catalyst used in hydrogenation benzene is due to impurity poisoning; particully, sulfur compounds which is usually present as impurities in the feedstocks. Generally sulfer compounds lower the activity of hydrogenation catalyst and the extent of poisoning depends on (1) the kind of sulfur compounds (2) the nature of catalyst (3) the experimental conditions of the experiment and (4) the organic compounds undergoing hydrogenation.

Emmett (1957) studied the poisoning action of several compounds for the hydrogenation of benzene over nickel at room temperature and reported that with 3 g. of nickel the rate of hydrogenate was decreased 50 % by the indicated amounts of each of the following materials:

thiophene	0.6	mg.
ethyl bromide	1	mg.
chrolobenzene	3	mg.
bromobenzene	15	mg.
water	100	mg.

Gonzalez-Tejuca, et al. (1977) determined the stoichiometry of adsorption for various poisons on Pt/Al_2O_3 and Pt/SiO_2 catalysts for hydrogenation of olefins and benzene at relatively low temperatures. H_2S and COS were found to deactivate one platinum site per molecule adsorbed, whereas CS_2 generally deactivated two platinum sites per adsorbed molecule. Not only was CS_2 found to deactivate more sites per molecule than the other poisons, it was also quite strongly adsorbed at 273-293 K. Indeed, the order of increasing reversibility was $H_2S = CS_2 < COS <$ thiophene. Infact, under the conditions studied thiophene was so easily desorbed that it was not an effective poison for Pt, that reverse to the result of Ni catalyst.

Zrncevic and Gomzi (1982) studied the deactivation of nickel on silica-alumina catalyst containing 21 % Ni during the hydrogenation of benzene. They found that deactivation on nickel on silica-alumina catalyst is due to a reduction in the number of active sites. The activity of catalyst decreases linearly with increases in the amount of poison until greater part of the catalyst has been deactivated. The rate of catalyst deactivation can be represented by first order kinetics, and activated energy for deactivation was 5.32 kJ/mol.

It was also found by the same authors that rate of catalyst deactivation decreases with increasing benzene and hydrogen partial pressure which suggests competition between reactants and poison for the same catalytic active centers. This means that benzene and hydrogen are adsorbed on the catalyst surface and that the dual-site adsorption model Langmuir-Hinshelwood for benzene hydrogenation is suitable to describe this reaction.

Markos and Ilavasky (1985) studied the poisoning of 58 % Ni/Al_2O_3 catalyst by thiophene during benzene hydrogenation. They found that the poisoning was irreversible under the reaction condition and the time for total deactivation depended on the temperature , space velocity, initial thiophene concentration and Ni particle size.

Zrncevic and Rusic (1985) found that the deactivation of $Ni-SiO_2-Al_2O_3$ catalyst by thiophene in the hydrogenation at 240-730°C and 1 atm was minimized by maintaining the hydrogenation temperature at 253°C.

Later, Masagutov, et al. (1988) investigated the poisoning effect of thiophene to Ni catalyst, they suggested that the deactivation of this catalyst was due to the poisoning on site for benzene adsorption.

Further studies was conducted by Seoane, et al. (1989), hydrogenation of ethylbenzene was used as a model reaction to study the effect of sulfur compounds to the activity of Ni/mordinite catalyst. The reaction was carried out in fixed-bed tubular reactor at 3 MPa, molar H_2/ETB =10 , 100-200°C and liquid space velocity between 1.5 and 20 hr^{-1}. From this study, they found that the addition of 100 ppm thiophene into the feed caused a sharp continuous drop of activity and affected the selectivity of the reaction, due to the presence of thiophene modified the yield of cracking products.

Marecot, et al.(1992) also investigated the deactivation by sulfur compounds on nickel catalysts in the course of benzene hydrogenation at low temperature (50-150°C) and atmospheric pressure in a conventional flow reactor. Various poisons were injected by pulse and were characterized by thier \`initial toxicty' T_i which was defined as the number of accessible metal atoms deactivated through adsorption of the first molecule of poison. The results show that the initial toxicity of thiophene depends strongly on the nature of catalyst since it varies from 0.4 to 7.0 nickel atoms deactivated by one molecule of poison when various type of catalyst are used (described in ref.18) ; furthermore, the initial toxicity of thiophene decreases as the temperature of reaction increases. This evalution is in accordance with the lower toxicity of thiophene when it is hydrogenolyzed since hydrogenolysis reactions are highly activated as the temperature increases.

These authors also found that initial toxicity of sulfur depends on the nature of sulfur compounds. The sulfur compounds examined in this work were thiophene, thiolane, hexane-thiol, propane-thiol and hydrogen sulfide. They found that $T_{i\ \text{thiophene}} \sim T_{i\ \text{thiolane}} > T_{i\ \text{propane-thiol}} \sim T_{i\ \text{hexane-thiol}} > T_{i\ H2S}$. The lowest toxicity of linear thiols compared to cyclic sulfur compounds can be explained by their higher dissociation accompanied by evolution of alkanes. On the other hand, this decomposition is accounted for the comparable toxicity of the linear thiols whatever their chain length is. This results is different to that of Maxted and Evans (1937) , whose investigation of the liquid phase hydrogenation of crotonic acid on nickel at 50°C, who found the relative toxicity of sulfer compounds to increase, in the following order: H_2S, CS_2, thiophene and cysteine, with increasing molecular size. The lowest toxicity of H_2S compared to the other sulfur compounds can be explained by the adsorption of the sulfur atom on one or two superficial nickel atoms while, for instance, thiophene which does not decompose can interact with five nickel atoms per molcular adsorbed.

The poisoning effect on hydrogenation of benzene by nitrogen compounds has also been investigated by a number investigators, Pluynin and Leonenko (1976) studied the effect of these compounds of petroleum oil on the liquid phase hydrogenation of benzene on Raney nickel. They found that nitrogen compounds irreversibly deactivated the Ni catalyst. The calculated adsorption coeffients of C_6H_6 and of N-containing compounds and the effective hydrogenation rate constants of C_6H_6 alone and in the presence of N compounds, showed that the latter block mainly the active center of C_6H_6 adsorption-donor-acceptor compounds which were formed on the catalyst surface. The poisoning of catalyst decreased with increase of N atom shieiding in the molecule of nitrogen compounds.

Gultekin and satterfield (1984) also reported the inhibition of aromatic hydrogenation by sulfur and nitrogen compounds. The reaction condition was 375°C and 69 atm, they found that the pseudo-first-order rate constant for propylbenzene hydrogenation decreased by a factor of 7 when the ammonia partial pressure increased from 0 to 0.13 atm,which was equal to the propylbenzene in the feed. Ammonia was thus a stronger inhibitor of hydrogenation than hydrogen sulfide, as the latter reduced the pseudo-first-order rate constants by the factor of only 2.3.

Barbier, et al. (1979) investigated the structural sensitivity of the poisoning of several reactions on Pt/Al_2O_3 catalysts with metal percentage exposed ranging from 5 to 80 %. Results for NH_3 poisoning of benzene hydrogenation are shown in Figure 2.1. While this reaction on clean Pt is a widely cited example of structure-insensitive tranformation, clearly it becomes structure-sensitive upon progressive poisoning of the Pt by ammonia, since the smaller metal particles deactivate more rapidly than larger ones. The authors proposed interpretation of such results on the basis of a heterogeneous surface with nonuniform poison adsorption. However, another possible explanation is that benzene chemisorption requires an ensemble of sites so that a single NH_3 molecule would be more effective poison on smaller crystallizes.

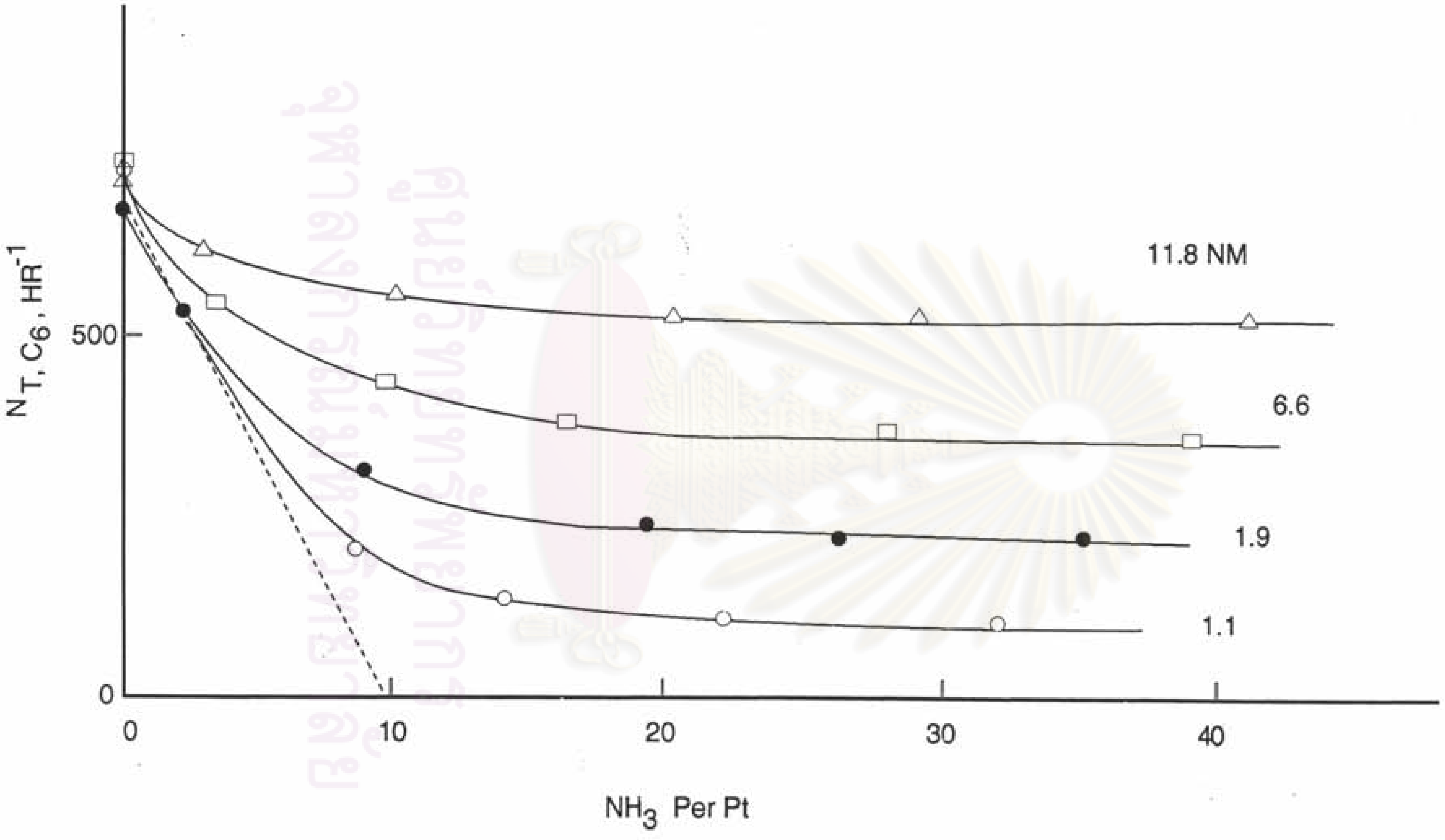


FIGURE 2.1 Effect of Pt Particle Size on the NH_3 Poisioning of Benzene Hydrogeneration.

2.6 Nitrogen compounds

Nitrogen compounds are present in most crude oil in smaller concentrations than sulfur compounds. The weight ratio N/S varies from about 1:2 in some high-nitrogen crudes to 1:5 to 1:10 in other crudes. Its concentration is usually less than 0.2 %, though it may be as high as 1.6 % in some crudes. Nitrogen compounds are concentrated in the high boiling fraction and in the residuum; very little is contained in the fraction that boils below *ca.* 300°C. It is present largely in the form of heterocyclic compounds having five or six-membered rings, mostly unsaturated. The nonheterocyclic compounds include anilines, aliphatic amines, and nitriles. The heterocyclic and other nitrogen compounds are often grouped into strong bases (quinoline, pyridine, acridine) versus weak bases or nonbasis compounds (indole, pyrrole, carbazole). The strong basis compounds are of particular concern in acid-catalyzed reactions, catalytic cracking, since they will poison catalyst.

2.7 Literature summary

1. Hydrogenation of benzene can be carried out catalytically either in mixed liquid-vapor phase or in a complete vapor phase. Catalyst which can be used comprise the group VIII metal such as Pt, Pd, Ru, and Ni or active metal supported on the high area oxide support such as Al_2O_3, SiO_2. A commercial Raney nickel is also used.

2. The operating condition for hydrogenation of benzene depends on the catalyst used. In general, the

pressure range from 100-1000 psig., and the temperature interval 200 30°C.

3. The reaction order of benzene hydrogenation was zero-order with respect to benzene and first order with respect to hydrogen.

4. Catalyst used in hydrogenation can be deactivated by impurity poisoning (such as sulfur, nitrogen, oxygen compounds) contained in feedstocks. These compounds have unshared electron pairs which facilitates the chemisorption process and can adsorb on the active sites of the catalyst. Thus, retarding the reactant to adsorb on the active sites and reduce the activity of catalyst.

5. Deactivation of catalyst used in hydrogenation of benzene was occured due to sulfur poisoning and the extent of poisoning depending on (1) the kind of sulfur compounds, (2) the amount of sulfur compounds, (3) the nature of catalyst, and (4) the experimental conditions of the experiment.

6. Nitrogen compounds was also suspected to deactivate catalyst used in benzene hydrogenation. However, there was a few observations on the effects of these compounds to benzene hydrogenation.