CHAPTER II

LITERATURE REVIEWS

2.1 Hydrodenitrogenation Reaction

Hydrodenitrogenation is a reaction between organonitrogen compounds and hydrogen gas, in the presence of a suitable catalyst and under suitable optimum conditions, converting to ammonia and hydrocarbon compounds without nitrogen element. Many researches have been conducted in its reaction and applications in petroleum industries. Aboul-Gheil and Abdoul (3) studied hydrodenitrogenation of a heavy gas oil fraction over a NiW/alumina catalyst at 25-100 atm pressure in H and 350-400 °C for 6 hr. The different N types found in these fraction have a resistance decreased to denitrogenation in the following order: non basic < weakly basic < strongly basic N compounds. Most of the N compounds present in the higher boiling fractions were dealkylated to lower boiling N compounds.

Nitrogen compounds founds in petroleum fractions can be grouped into three catagories:

1. Aliphatic aromatics and amines.
2. Basic heterocyclic compounds of the pyridine and quinoline type.
3. Non-basic heterocyclic compounds of the type pyrrole, indole, and carbazole type.

Table 2.1 presents some hydrogenolysis reaction of petroleum nitrogen compounds.

Hydrodenitrogenation reaction is a stepwise process with hydrogenation of the N containing ring as a 1st-step (4, 5, 6, 7) followed by hydrogenolysis of the C-N bond. Hydrogenation of the heteroring is required to reduce the energy of the C-N bonds. The energies of carbon-nitrogen single and double bonds are 73 and 147 kcal/mol, respectively (8). The requirement that ring hydrogenation occur as a 1st-step also implies that the position of the equilibrium of the hydrogenation reactions can affect nitrogen-removal rates if the rates of hydrogenolysis reaction are lower than the rates of hydrogenation.

2.2 Hydrodenitrogenation Catalysts

In hydrodenitrogenation reaction, catalysts are used for reducing activated energy of the reaction. Because the reactions have two mechanisms: hydrogenation and hydrogenolysis, the catalyst used in these reactions is usually a bifunctional catalysts having the proper balance of both hydrogenation and hydrogenolysis functions (9).

Catalysts used in hydrodenitrogenation reaction consist of transition metal group VIII, Ni or Co, as promoter metals and group VIB, Mo or W. These metals were impregnated on the support such as alumina, active carbon or silica (10, 11). Cobalt and nickel do not provide significant activity when present alone, but the activity

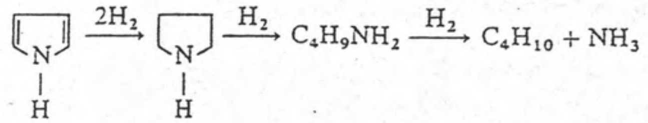
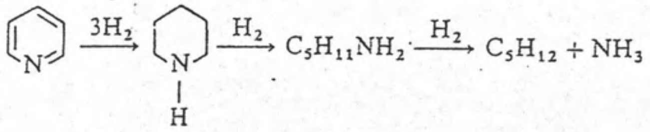
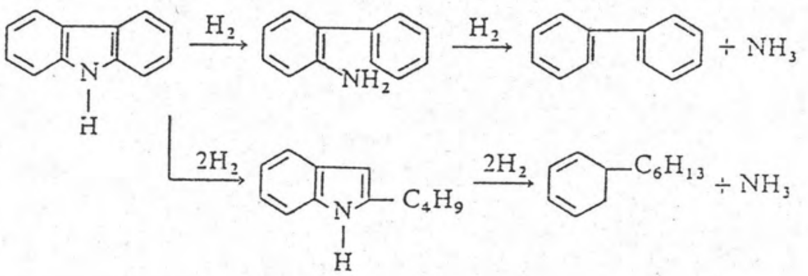
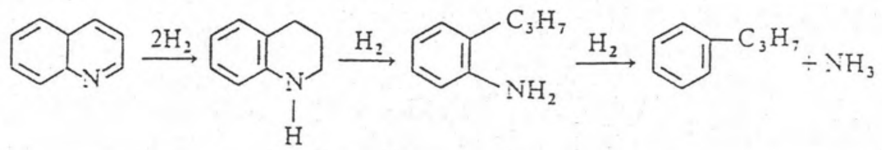
Amines	$R-NH_2 \xrightarrow{H_2} RH + NH_3$
Pyrrole	
Pyridine	
Carbazole	
Quinoline	

Table 2.1 Hydrogenolysis Reaction of Petroleum Nitrogen Compounds [1]

is increased when combined with molybdenum or tungsten. Tungsten catalysts are typically promoted with nickel and molybdenum catalysts with nickel or cobolt. Because they are more expensive than NiMo or CoMo catalysts, nickel-tungsten catalysts are used primarily for special applications.

The HDN catalysts must be converted to proper sulfided state before used in order to achieve the desired activity and selectivity (9, 12). A minimum concentration of hydrogen sulfide must be presented in the reaction to maintain the catalyst in the sulfide form (13). The sulfide NiMo increased the rate of ring hydrogenation and the C-N bond scission whereas the sulfide CoMo catalysts accelerated the C-N bond scission but no effect on the ring hydrogenation. The sulfide CoMo catalysts increased the rate of N removal in a 10-fold in comparison with the oxide form (12). Ledoux and Djellouli (19) found that NiMo was 2.5 times more active than Mo and CoMo in the presence of sulfur and these catalysts exhibit the same activity in the absence of sulfur.

The effect of catalyst composition such as NiMo, CoMo, and NiW/alumina in hydrogenation of quinoline and acridine was reported (14, 15, 16, 17, 18, 20, 24, 25). They found that NiMo and NiW/alumina catalysts were more active for the HDN of model compounds than CoMo/alumina catalys, while Horita et al. (26) found that the catalysts with high HDN activity were NiMo. The HDN activity decreased in the following order: NiMo > NiCoMo = CoMo > NiW. Nickel-molybdenum and NiW give about double the rate of hydrogenation than CoMo does. Nickel catalysts gave a greater degree of hydrogenation of aromatic, unsaturation, and denitrogenation of the raw material than CoMo catalyst. The ratio of NiMo and NiW changed had only a denitrogenation activity of the catalyst. The optimum activity of the NiMo catalysts for hydrodenitrogenation occurs at a Ni/(Ni+Mo) at a ratio about 0.4 while that of the NiW catalysts occurs at a Ni/(Ni+W) at a ratio of about 0.5.

The effect of an acidic support on simultaneous hydrodenitrogenation of heterocyclic nitrogen such as CoMo/silica-alumina, CoMo/alumina, NiW/silica-alumina, and NiW/alumina were obtained by Moore et al. (21) and Aboul-Ghiet (22) who found that silica-alumina support was more effective support for HDN than alumina. However, Krichko et al.(23) found that the best promoter for the N removal were Co and Ni promoted on zeolite catalysts. Moreau et al. (42) found that NiMo catalysts supported on ZrO_2, TiO_2, and Ni aluminate had similar or slightly better activity for HDN than the commercial alumina-supported catalysts.

In 1988 the catalytic features of molybdenum, iron, and nickel catalysts in hydrodenitrogenation and hydrocracking were studied by Hattori et al.(27). The hydrodenitrogenation activity order of a model N-compound carbazole, was Ni catalysts> Mo catalysts> Fe catalysts and was affected by sulfiding and support. This result was supported by Hattori et al.(28) who found that sulfidation increases the Fe-based catalysts activities but decreases the activities of the Ni- and Mo-based catalysts in hydrodenitrogenation and hydrocracking.

Molybdenum catalysts was studied in its activity and selectivity for coal liquefaction reaction by Curtis and Pellegrino (29). The Mo catalysts used were Mo naphthenate, Mo/alumina, amd MoS_2. They suggested that the Mo naphthenate was most active for hydrocarbon production and removal of N compounds than Mo/alumina and MoS_2. Sajkowski and Oyam (30) found that the performance of Mo_2C and Mo_2N catalysts was 3-5 fold better than a commercial sulfided NiMo catalysts.

Harvey and Matheson (31) studied the hydroprocessing catalysis by supporting ruthenium sulfide. Ruthenium was supported on Y-zeolite and alumina which compared in HDN activities with a conventional NiMo/alumina. They found that ruthenium sulfide supported on Y-zeolite highly enhanced activity of HDN. Ruthenium promoted CoMo catalysts for coal liquids exhibited enhanced quinoline HDN activity and these catalysts increased 5-fold selectivity to aromatic hydrocarbon products (32).

The 1st-, 2nd-, and 3rd-row transition metal sulfides supported on activated C were studied for the hydrodenitrogenation activity (33, 34, 35). The activity of these catalysts decreased in the following order of tranition metals: 3rd-row (Re, Pt, Os, Ir) > 2nd-row (Mo, Pd, Ru, Rh) > 1st-row (Cu, Mn, Fe, Co, Ni). Rhenium sulfide in the hydrodenitrogenation of a model N-compound had a very high selectivity for propylbenzene.

Ledoux and Djellouli (36) studied the hydrodenitrogenation activity and selectivity of well-dispersed transition metal sulfides of the second row on activated carbon and a conventional NiMo/alumina sulfide catalyst. They classified these catalysts into 3 groups following their HDN activity: the very poor catalysts such as NiMo, Zr, Ag, and Nb, the active catalysts such as Mo, Rh, and Pd, and the very active catalysts Ru. These transition metals such as Co, Rh, and Ru were more active but less selective for the HDN conversion than supported metal sulfides (37). Carbon-supported sulfides of Pt were more better HDN catalysts than the commercial bimetallic catalysts. The Rh, Ru, and Pd catalysts had HDN selectivity similar to the selectivity of the NiMo and CoMo catalysts but the Ir and Pt catalysts were extremely selective for HDN (38).

Comparison of carbon and alumina supported nickel-molybdenum sulfide catalysts in hydrodenitrogenation was studied by Hillerova et al.(39) and Drahoradova et al. (40). The C-support used was based on carbon black. They found that the C-supported catalysts had hydrodenitrogenation activity and selectivity 3-5 times higher than alumina-supported catalysts.

2.3 Hydrodenitrogenation of Quinoline

2.3.1 Thermodynamics

Nitrogen removal from quinoline requires hydrogenation of the ring containing the nitrogen atom as the first step followed by hydrogenolysis of C-N bond. The first step is too fast to measure whereas the second step is the slowest. Therefore, the latter is the rate limiting step (5, 75, 76). The requirement of ring hydrogenation occurs before nitrogen removal implies that it is required to reduce the relatively large energy of the C-N bond. Therefore, the position of the equilibrium of the hydrogenation reaction can affect nitrogen-removal rates if the rates of the hydrogenolysis reaction are significantly lower than the rates of hydrogenation.

Equilibrium constant of quinoline and its products are shown in Table 2.2.

These equilibrium constants were calculated from the standard Gibbs free energies of formation at 1 atm. The equilibrium constants are less than unity for ring saturation and become smaller with increasing temperature, as the ring hydrogenations are exothermic. Satterfield et al.(79) found that quinoline was converted rapidly and completely to PyTHQ at lower temperatures. PyTHQ was then converted either to OPA or to DHQ. At higher temperatures the concentration of quinoline was much less than that of BzTHQ and subsequently to DHQ and its products.

Furthermore, Cocchetto and Satterfield (78) reported that the saturation of the aromatic ring of quinoline to form BzTHQ (hence, also the dehydrodenation of DHQ to BzTHQ) was thermodynamically more favorable than saturation of the heteroring to form PyTHQ (or dehydrogenation of DHQ to PyTHQ). In addition it was found that at a constant hydrogen partial pressure, the equilibrium concentration of BzTHQ or PyTHQ proceeds through a maximum as temperature increases, but this maximum shifted to lower temperatures with decreasing hydrogen partial pressure.

Table 2.2 Equilibrium Constants for Nitrogen-Removal Reactions in The Quinoline Reaction Networks*

	lok K at		H_o,rxn kcal/mol of organic reactant
	300 °C	400 °C	
$Q + 2H_2$ ----> PyTHQ	-1.4	-3.2	-32
$Q + 2H_2$ ----> BzTHQ	-0.7	-3.0	-41
PyTHQ + $3H_2$ ----> DHQ	-2.8	-5.4	-46
BzTHQ+ $3H_2$ ----> DHQ	-3.5	-5.6	-37
PyTHQ + H_2 ----> OPA	4.3	3.0	-2
DHQ + $2H_2$ ----> PCH + NH_3	6.3	7.9	-28
OPA + H_2 ----> PB + NH_3	6.0	5.6	-7
$Q + 4H_2$ ----> PB + NH_3	7.0	3.3	-65

* From Cocchetto and Satterfield (77, 78)

2.3.2 Reactivities

The conversion of quinoline will be distinguished from its HDN conversion, i.e. giving propylbenzene or propylcyclohexane and ammonia. Because quinoline must first be hydrogenated before the nitrogen is removed, there are numerous intermediate products that contain nitrogen. The rates of HDN of quinoline are shown in Table 2.3.

The comparison of the reactivities is rough because of differences in initial reactant concentrations and these affect the HDN rate because of strong self-inhibition by nitrogen compounds. Bhinde et al.(87) studied the comparison of reactivities of basic and non-basic organonitrogen compounds in batch reactor at 350 °C 34 atm on a NiMo/alumina catalyst. They found that for indole and quinoline HDN, the pseudo-first-order constants being $4.19x10^{-5}$ and $3.81x10^{-5}$ L/(g of catalyst.S), respectively. The similar reactivities could arise because nonbasic organonitrogen compounds were converted to basic ones upon hydrogenation. However, additional data are needed to resolve these reactivity differrences between basic and nonbasic organonitrogen compounds, especially for higher molecular weight compounds such as carbazole.

2.3.3 Reaction Networks and Kinetics

Most of the quantitative network determinations with quinoline were conducted for liquid phase reactants (Table2.4). The network proposed by most investigators can be represented by that shown in Figure 2.1.

Table 2.3 Reactivities for the HDN of Quinoline*

Compound	Conc. in Feed wt %	Pseudo-first-order rate const. L/(g.cat.S)	Ref.
Quinoline	0.5	$3.18x10^{-5}$	87**
	1.0	$9.39x10^{-4}$	

* From Girgis and Gates (96)

* Batch reactor, 350 °C, 34 atm, NiMo/alumina catalyst, n-hexadecan solvent.

**Batch reactor, 376 °C, 136 atm, NiMo/alumina catalyst, paraffinic white oil solvent.

Table 2.4 Reaction Conditions in HDN Network Investigation

Conditions	Reference
batch reactor, 0.1-1 wt% quinoline in paraffinic white oil, 300-375 °C, 21-136 atm, NiMo/alumina catalyst	80, 87
vapor-phase reactant, 330-420 °C, 35 and 69 atm, NiMo/alumina catalyst	83, 85
trickle-bed reactor, 1-5 wt% quinoline in paraffinic white oil, 350-390 °C, 69 atm, NiMo/alumina catalyst	81, 86
trickle-bed reactor, 2-13 wt% quinoline in paraffinic white oil, 330 and 375 °C, 69 atm, NiMo/alumina	97
batch reactor, 0.47-0.57 wt% quinoline in n-hexadecane solvent, 350 °C, 10-150 atm, NiMo/alumina catalyst	82

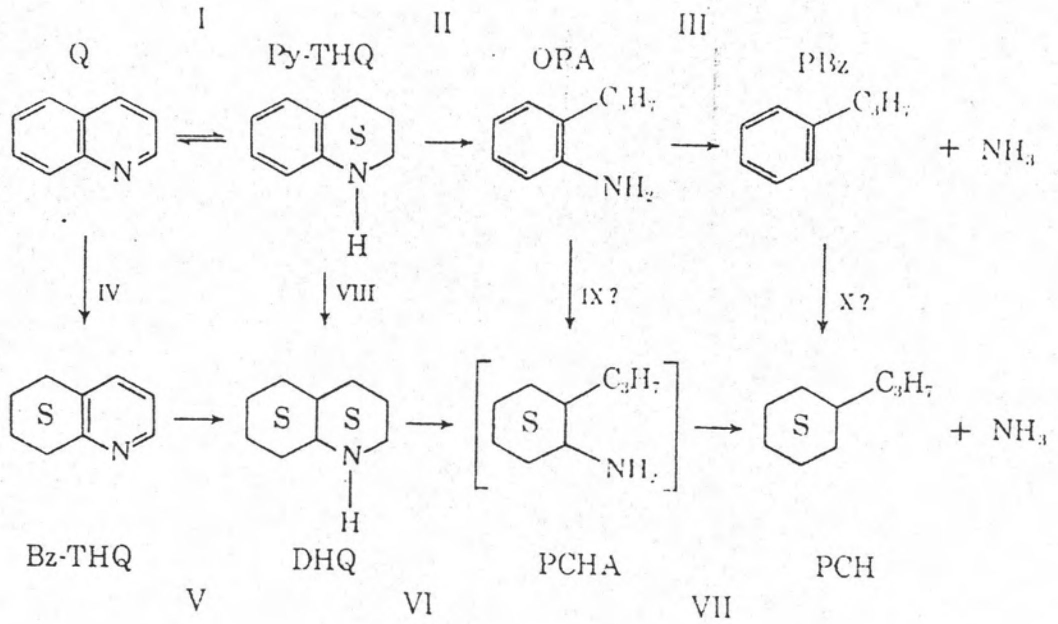


Figure 2.1 Reaction Network of Quinoline HDN
Proposed by Satterfield et al. [79]

Quinoline HDN requires hydrogenation of one or both rings followed by hydrogenolysis of C-N bonds. The networks are two pathway: one involves the successive formation from quinoline of 1,2,3,4-tetrahydroquinoline (PyTHQ), o-propylaniline (OPA), and then n-propylbenzene and ammonia. These are shown as steps I, II,and III in Figure 2.1. A second pathway involves the successive formation from quinoline of 5,6,7,8-tetrahydroquinoline (BzTHQ), decahydroquinoline (DHQ), propylcyclohexylamine (PCHA), and then ammonia and propylcyclohexane (PCH), shown as steps IV, V, VI, and VII in Figure 2.1.

Hydrogenation of quinoline to PyTHQ is much more rapid than to BzTHQ. The principle pathway for hydrodenitrogenation of quinoline under industrial processing conditions was via decahydroquinoline. The principle hydrocarbon product was propylcyclohexane. These results were supported by Shih et al.(80) who found that hydrogenolysis of PyTHQ to give OPA was slower than its hydrogenation to give DHQ. They concluded that the slow hydrogenolysis of PyTHQ could be due to the resonance interaction between the benzenoid ring and the nitrogen lone-pair electron. Most of the nitrogen removal proceeds via decahydroquinoline, with the pathway through 5,6,7,8-tetrahydroquinoline dominating. The quinoline HDN rate increased with hydrogen partial pressure, but the hydrogen consumption for a given HDN conversion also increased with pressure because of the increasing contribution to the overall HDN of the pathway through decahydroquinoline (Figure 2.2).

They suggested that all nitrogen-containing

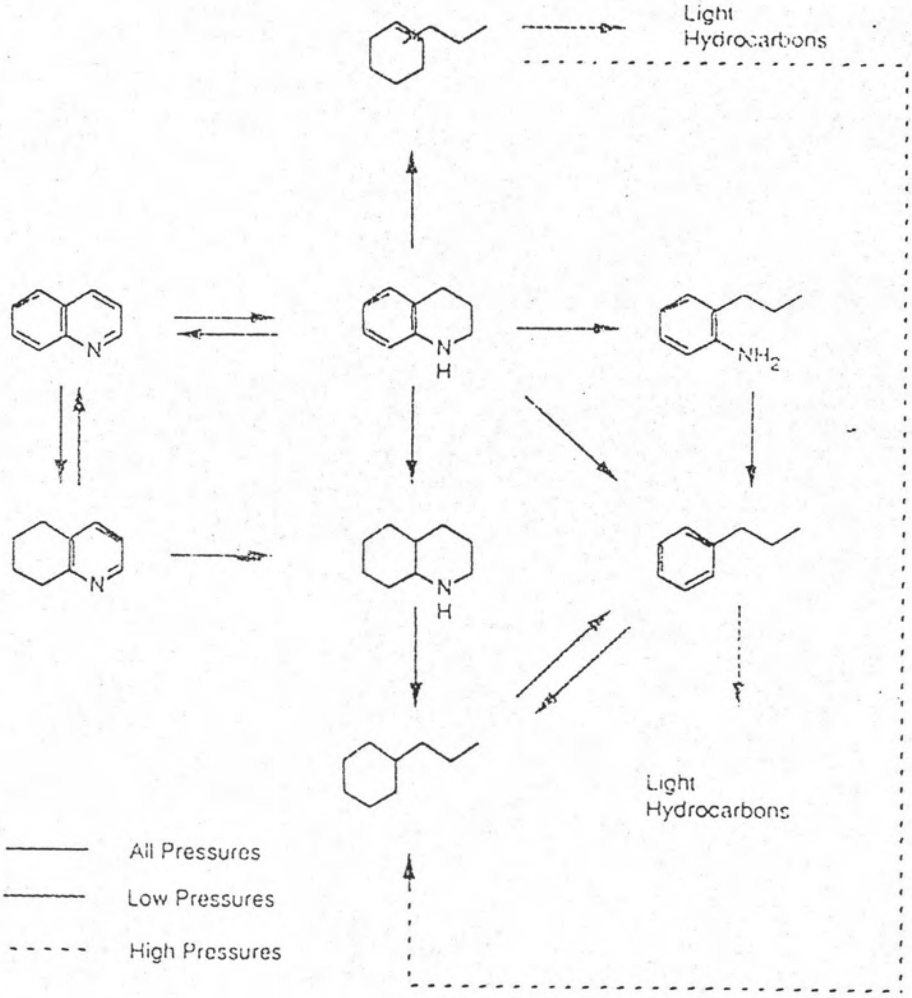


Figure 2.2 Reaction Network of Quinoline Proposed by Gioia and Lee (82)

molecules, including ammonia, were assumed to have the same adsorption parameter because the reactions of the quinoline network followed pseudo-first-order kinetics at a given feed quinoline concentration. The pseudo-first-order rate constants were correlated with a Langmiur-Hinshelwood rate form (Table 2.5). The 100-fold differences in adsorption parameters for the nitrogen compounds on each site were consistent with the two-site assumption.

Satterfield and Yang (81) compared the HDN of quinoline in a vapor phase and a liquid phase reaction. In the vapor phase, hydrogenation reactions slightly faster but hydrogenolysis reactions slightly slower than in the liquid phase. Hydrogen might adsorb more readily from a vapor phase than from a liquid phase. A steady state structure of the sulfided catalyst might be slightly different in vapor phase and liquid phase operation. The path of high hydrogen consumption was thus favored kinetically. They were able to quantify the inhibition by each of the organonitrogen intermediates in the network. They were able to quantify the inhibition by each of the organonitrogen intermediates in the network. A one-site Langmiur-Hinshelwood-type kinetic was used for both hydrogenolysis and hydrogenation reactions (Table 2.5). The basic asuumption was that all the molecules compete with each other to be adsorbed on active sites on the catalyst surface for both hydrogenation and hydrogenolysis. The term of unity that typically appears in the denominator of a Langmiur-Hinshelwood expression was neglected becuase it was assumed that

Table 2.5 Rate Equation Proposed in Quinoline Reaction Network Investigations*

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1. Shih et al.(80)

A. Hydrogenation

$$r_{ij} = k'_{ij}C_i = \frac{k_{ij}P_{H2}^{\,2}C_i}{(1 + K_{H2}P_{H2} + K_NC_{N0})^2}$$

Adsorption parameter values at 342 °C are as follows:

$K_{H2} = 0.05$ atm^{-1}

$K_N = 6.4\text{x}10^8$ g of oil/mol

B. Hydrogenolysis

$$r_{ij} = k'_{ij}C_i = \frac{k_{ij}P_{H2}^{\,n}C_i}{(1 + K_{H2}P_{H2} + K_NC_{N0})^2}$$

where n equal 1 and 0 for the respective hydrogenolyses of 1,2,3,4-tetrahydroquinoline and decahydroquinoline.

Adsorption parameter values at 342 °C are as follows:

$K_{H2} = 0.05$ atm^{-1}

$K_N = 6.4\text{x}10^6$ g of oil/mol

Table 2.5 (continue)

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2. Satterfield and Yang (81); Yang and Satterfield (86):

$$r_{ij} = \frac{k_{ij}K_iC_i}{K_{AA}C_{AA} + K_{SA}C_{SA} + K_AC_A}$$

$K_{SA}/K_{AA} = 2$

K_A/K_{AA} 0.7

The subscripts A, SA, and AA denote ammonia, decahydroquinoline, and aromatic amines, respectively; quinoline, 1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline, and o-propylaniline comprise the aromatic amines, and assumed to have Table 5. The same adsorption paramater K_{AA}. C_{AA} denotes the sum of the concentrations of the aromatic amines. Adsorption parameter ratios are assumed temperature independent.

3. Miller and Hineman (97):

$$r_{HDN} = \frac{kC_N}{1 + K_NC_N}$$

Respective adsorption parameter values at 330 and 375 °C are

$K_N = (7.9\text{-}9.6)\text{x}10^4$ g of oil/mol

$K_N = (1.7\text{-}2.3)\text{x}10^4$ g of oil/mol

Table 2.5 (continue)

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4. Gioia and Lee (82):

$$r_{ij} = \frac{k_{ij}C_j}{1 + K_1C_1 + K_2C_2}$$

where the subscripts 1 and 2 denote quinoline and 1,2,3,4-tetrahydroquinoline, respectively.

Adsorption parameter values at 350 °C are as followed:

$K_1 = K_2 = 10^5$ g of oil/mol

Variation of the rate constants with the hydrogen partial pressure is given by

$$k_{ij} = \frac{k'_{ij}P_{H2}^{\,m}}{1 + K_{H2}P_{H2}}$$

with m = 0 for dehydrogenation reactions and m = n = hydrogen stoicheometric coefficient for hydrogenation reactions.

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all sites were covered by the organonitrogen compounds under reaction conditions. All nitrogen compounds in the reactions were assumed to adsorb and were grouped into three groups according to their basicities (Table 2.5).

Gioia and Lee (82) found the pathways for nitrogen removal in addition to those shown in Figure 2.1 (Figure 2.2). The additional reactions are shown in Figure 2.2 giving light hydrocarbons were assumed to occur because good mass balances could not be obtained at lower pressure. At large H pressure, the hydrodenitrogenation process was faster than lower H pressure but more hydrogen was required. Furthermore the kinetic analysis indicated that bond rupture reactions were not rate controlled by hydrogenation except at very low pressure. Mechanistic evidence was not offered for the reaction in which PyTHQ was converted to PB and PCH. However, good fits to the data were obtained only when it was asuumed that these two reactions occured. The kinetics of the reactions in the quinoline network and the overall HDN have been modeled with Langmiur-Hinshelwood rate expressions.

The effect of hydrogen pressure on the rate of each reaction was estimated by fitting to determine each of pseudo-rate constants k_{ij} as shown in Table 2.5. Only an order of magnitude estimate could be obtained for the adsorption parameters. The order of magnitude of K_1 and K_2 which fits the data was 10^5 g/gmol for both. The appearance of only two species in the denominator was also consistent with the fact that these were the most polar among the species involved and, therefore, possibly they were most readily adsorbed.

They found that pseudo-rate constants corresponding to hydrogenation and dehydrogenation reactions increased and decreased, respectively, with hydrogen partial pressure. The pseudo-rate constants corresponding to hydrogenolysis reactions did not vary with hydrogen partial pressure.

Satterfield and Cocchetto (83) assumed that hydrogen and the nitrogen compounds adsorb on differenct catalyst sites, as suggested by adsorption measurements and other reaction studies (84). Sonnemane et al.(84) found that pseudo-first-order kinetics were inadequate because of the strong competitive adsorption of the nitrogen compounds. The secondary amine intermediate, decahydroquinoline, was the most strongly adsorbed, but the relative values for the several compounds were not greatly different, being equal within a factor of 3 (83).

Satterfield and Gultekin (85) also quantified the effect of hydrogen sulfide on hydrogenation and hydrogenolysis step in the quinoline network. Hydrogen sulfide was produced in situ from carbon disulfide added to the feed. They found that in the presence of H_2S, the hydrogenation and dehydrogenation rate constants were decreased by about 10 to 15 %. The hydrogenolysis reaction were markedly enhanced by the presence of H_2S, by a factor of 2 - 5. These results led them to proposed that these reactions occured on two different types of sites, but only one type of catalytic site was assumed in their kinetic model. Hydrogenation reactions might be retarded by competitive adsorption between H_2S and nitrogen compounds for hydrogenation sites. The enhancement in hydrogenolysis reactions might be caused by an increase in the surface acidity from the H_2S.

To explain the effect of H_2S on the network of quinoline, Yang and Satterfield (86) postulated the existence of two kinds of catalyst sites on a sulfided NiMo/alumina catalyst. Site I was a sulfur vacancy associated with the molybdenum atom that sulfur vacancies were responsible for most hydrogenation and possibly hydrogenolysis reactions. Site II was a Bronsted acid sites by which they were responsible for hydrogenolysis reactions. Figure 2.3 shows the interaction of H_2S with catalyst. Similar conclusions with the idea of separate sites for hydrogenolysis and hydrogenation were reached by Satterfield and Cocchetto (83).

In addition, Satterfield and co-workers (refernces are cited in Table 2.4) proposed that the carrier solvent reduced the differences in the adsorption parameters for liquid-phase reactants because of the ratios of K_S/K_{AA} and K_A/K_{AA} (terms are definded in Table 2.5) were found to be 2 and 0.7, respectively, with the liquid-phase reactants; for comparison, the value are 6 and 0.25 for the vapor-phase reactants, respectively.

2.4 Effects of Additives on the HDN of Quinoline

2.4.1 Aromatic Hydrocarbon

The study to the inhibition of both the hydrogenolysis and the hydrogenation reactions of the quinoline HDN by aromatic hydrocarbon was minimal, such

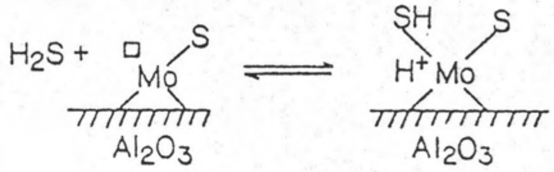

Figure 2.3 Interaction of H_2S with Catalyst Proposed by Yang and Satterfield (86)

as Bhind et al.(87). When 5.9 wt% naphthalene was added to a feed containing 0.2 wt% quinoline in hexane, they found that the pseudo-first-order rate constants for quinoline network were lower by 10-15 %. This results led them to propose that the inhibition parameters for naphthalene and its hydrogenation products were 2 order of magnitude smaller than those for ammonia and the organonitrogen compounds in the quinoline network.

2.4.2 Sulfur Compounds

Many studies found that sulfur compounds were also weak inhibitors of HDN. Pseudo-first-order rate constants for the quinoline network which were determinded by Bhind et al.(87) were almost unchanged when feeds containing 0.5 wt% quinoline were added by 0.7 wt% dibenzothiophene. For the hydrogenolysis of decahydroquinoline, they found that pseudo-first-order rate constant was increased only 25 % from the effect of dibenzothiophene.

The effect of hydrogen sulfide on the HDN of quinoline was studied by Satterfield and co-workers (85, 86, 88, 89, 90) and Gultekin et al. (91, 92). Satterfield and co-workers and Gultekin et al. found that hydrogen sulfide slightly inhibits hydrogenation reactions but markedly accerelates hydrogenolysis reactions. The overall effect was to enhance the HDN of quinoline. The accerelating effect of H_2S on the HDN rate reached a plateau value, under the reaction condition studied, when the H_2S partial pressure was increased to a value corresponding to about a 1 : 1 mole ratio with the quinoline feed. The effect of H_2S had not been presented in term of Langmiur-Hinshelwood rate expression, but if the effect of H_2S was to modify the catalytic surface in some way, then such a simple rate expression would not be appropriate. The activation energies for the hydrogenation and dehydrogenations were not markedly affected by the presence of H_2S (generated in situ from CS_2), but those for the hydrogenolysis reactions were significantly reduced (86).

Satterfield et al.(93, 94) speculated that hydrogen sulfide kept the catalyst in a sulfide state (no other source of sulfur was present in the feed), or perhaps the hydrogen sulfide aided in removing basic nitrogen compounds from the surface. Yang and Satterfield (86) postulated that hydrogen sulfide reduces the number of sulfur vacancies and increases the number of Bronsted acid site. They observed a slight reduction in the hydrogenation rates but a significant increase in the hydrogenolysis rates in the quinoline HDN network. Similar results were reported by Gultekin et al. (92).

2.4.3 Oxygen Compounds

Satterfield and co-workers (88, 89, 95) and also Gultekin et al.(90) investigated the effect of water generated in situ from decanol, on the HDN of quinoline. They found that the HDN of quinoline on a NiMo/alumina catalyst was increased in the presence of oxygen (hydrogen sulfide was either the presence or absence) as shown in Table 2.6.

Satterfield and Carter (95) found that in the absence of H_2S, water vapor had a little effect on overall HDN rate. The enhancement was less than that obtained with hydrogen sulfide in the absence of water. The presence of both H_2S and H_2O, there was a slight inhibition compared to the presence of H_2S alone. Removal of water from the feed, in the presence of H_2S, resulted in a more gradule decline in the HDN rate whereas removal of hydrogen sulfide from the feed resulted in a rapid decrease in the HDN rate (88).

Satterfield and Smith (89) also determined the effects of hydrogen sulfide and water addition on the HDN kinetics, assuming the rate expression is identical to those used earlier (Table 2.6). Figure 2.4 shows the simplified scheme used for kinetic analysis and Table 2.7 shows the effects of water and hydrogen sulfide on reaction rate constants.

As shown in Table 2.7, the addition of hydrogen sulfide enhanced the rates of some of the hydrogenation reaction as well as those of the hydrogenolysis reactions. With both water and hydrogen sulfide in the feed, the rate constants for all the reactions were larger than when either water or hydrogen sulfide alone was present. The enhancement of the hydrogenation and hydrogenolysis rates of both H_2S and H_2O suggested to be related to increased acidity of the catalyst surface.

Gultekin et al. (92) reported that in the presence of H_2S and/or H_2O, the hydrodenitrogenation activity of the oxide catalyst was enhanced. This effect was due to the increase of the catalyst acidity by the introduction of H_2S and part of the catalyst might be sulfided,

Table 2.6 Effect of Hydrogen Sulfide and Water on Quinoline HDN*

P_{H2O}, atm	P_{H2S}, atm	% Quinoline HDN
0	0	42
0.063	0	54
0	0.12	78
0.063	0.12	94

* From Satterfiel et al.(88); Satterfield and Smith (89)

** Conditions: 375 °C, 69 atm,
space time = 365 (g.cat.h)/(mol of quinoline)

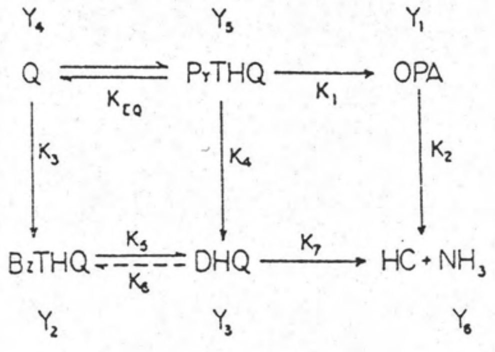

Figure 2.4 Simplified Scheme Used for Kinetic Analysis Proposed by Satterfield and Smith (89)

Table 2.7 Effect of Water and Hydrogen Sulfide on Reaction Rate Constants*

Rate constant	H_2O, %	H_2S, %	$H_2O + H_2S$, %
		Hydrogenation	
k_2	NC	17	42
k_3	NC	31	28
k_4	NC	NC	NC
k_5	NC	106	113
		Hydrogenolysis	
k_1	NC	300	300
k_2	20	167	197

Note: NC, no significant change. H_2S and H_2O each present at 14 kPa of partial pressure.

* From Satterfield and Smith (89)

which was more active than the oxide catalyst. The presence of H_2S also enhanced the acidity of the sulfide catalyst. However, the inclusion of water only had effect on the sulfide catalyst.

2.4.4 Nitrogen Compounds

Bhinde et al.(87) studied the effect of quinoline on indole HDN (Table 2.8). The pseudo-first-order rate constants were calculated for the indole network shown in Figure 2.5. The pseudo-first-order rate constants were decreased by one-third when 0.5 wt% quinoline was added to 0.5 wt% indole. However, They observed that the inhibition by quinoline of the reactions in the indole network was less severe than the inhibition of the reactions of the naphthalene network; in the latter case, the same amount of quinoline reduced the pseudo-first-order rate constants by an order of magnitude. They inferred that indole and its nitrogen-containing products were more strongly adsorbed than the aromatic hydrocarbons.

Furthermore, they also investigated the effect of indole on quinoline HDN. The pseudo-first-order rate constants in the quinoline network were compared in experiments with 0.5 wt% quinoline and the indole-quinoline mixture. The indole affected the pseudo-first-order rate constants by less than 10 %. This weak inhibition was attributed to the weaker adsorption by indole, which is nonbasic.

They studied the inhibition of reaction products of quinoline on quinoline conversion. Table 2.9 shows the concentration of the other reactants when the

Table 2.8 Reaction Conditions for Investigations of Inhibition of Quinoline HDN*

Reactant	Additive	Conditons	Reference
		1. Aromatic Hydrocarbons	
Quinoline 0.2 wt%	Naphthalene 0-5.9 wt%	batch reactor, 350 °C, 35 atm, n-hexadecane solvent, NiMo/alumina	87
		2. Sulfur Compounds	
Quinoline 0.5 wt%	Dibenzothiophene 0-0.7 wt%	batch reactor, 350 °C, 35 atm, n-hexadecane solvent, NiMo/alumina	87
		3. Oxygen Compounds	
Quinoline, Ethylaniline, 0.4 mmol/g	Ethylphenol, Ethylphenol, Benzofuran, Dibenzyl - ether, 0.4 mmol/g	trickle-bed reactor 375 °C, 69 atm, n-hexadecane solvent, NiMo/alumina	
Quinoline, 5 wt%	H_2O, H_2S, 0-0.12 atm	trickle-bed reactor, 375 °C, 69 atm, n-hexadecane solvent, NiMo/alumina	88, 89

Tabl 2.8 (continue)

		4. Nitrogen Compounds	
Quinoline, 0.5 wt%	Indol, Quinoline, 0.2-2 wt%	batch reactor, 350 °C, 35 atm, n-hexadecane solvent, NiMo/alumina	87

* From Girgis and Gates (96)

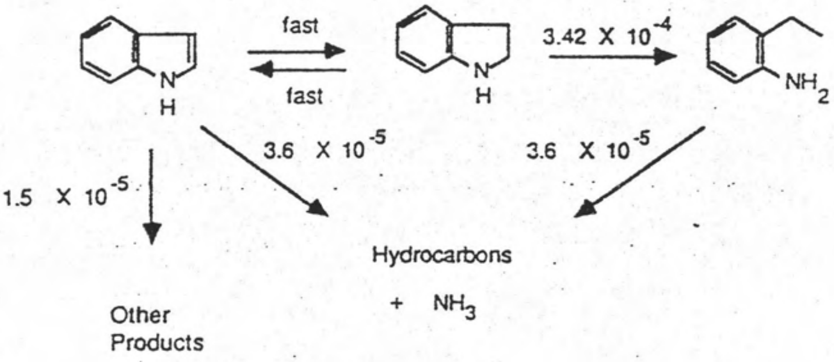

Figure 2.5 Indole Network
Proposed by Bhinde et al. (87)

quinoline concentration was varied from 0.2 to 2.0 wt%. The pseudo-first-order rate constants were decreased significantly with increasing quinoline concentration as shown in Table 2.9.

2.4.5 Mixtures of Sulfur, Oxygen, and Nitrogen Compounds

Gultekin et al.(90) investigated the combined effects of hydrogen sulfide, water, and ammonia on liquid-phase hydrodenitrogenation of quinoline in a batch slurry reactor on a presulfided NiMo/alumina catalyst at 7.0 MPa and 330, 350, 375 °C. They found that the kinetics of the overall HDN of quinoline were found to be 0.8 order with respect to total nitrogen concentration, whereas individual rates were first order. Since Q and PyTHQ were in equilibrium during the reaction, they proposed the kinetics model for the reaction network as shown in Figure 2.6. The combined effects of H_2S, H_2O,and NH_3 on each rate constant at 375 °C are shown in Table 2.10.

As shown in Table 10, the combined effects of H_2S, H_2O, and NH_3 were still complex; i.e., the hydrogenation rate constants decreased, while the hydrogenolysis rate constants increased considerably (R_1 = 1.42, R_5 = 1.38), and the net effect was the enhancement of the overall HDN (R_T = 1.14).

2.5 Deactivation of catalysts

Catalyst deactivation may be divided into 3

Table 2.9 Variation of Selected Pseudo-First-Order Rate Constants in L/(g of catalyst.S) for the Quinoline HDN Network for Various Feed Quinoline Concentrations

Reaction	Quinoline feed conc., wt%		
	0.2	0.5	2.0
Q + 2H_2 ---> BzTHQ + H_2	$3.2\text{x}10^{-3}$	$1.8\text{x}10^{-4}$	$7.8\text{x}10^{-4}$
Q ---> Hydrocarbon + NH_3	$6.7\text{x}10^{-4}$	$2.8\text{x}10^{-4}$	$9.7\text{x}10^{-5}$
DHQ $\xrightarrow{H_2}$ Hydrocarbon + NH_3	$7.5\text{x}10^{-3}$	$3.1\text{x}10^{-3}$	$1.5\text{x}10^{-3}$

Note: Reaction conditions are given in Table 2.8

* From Bhinde (87)

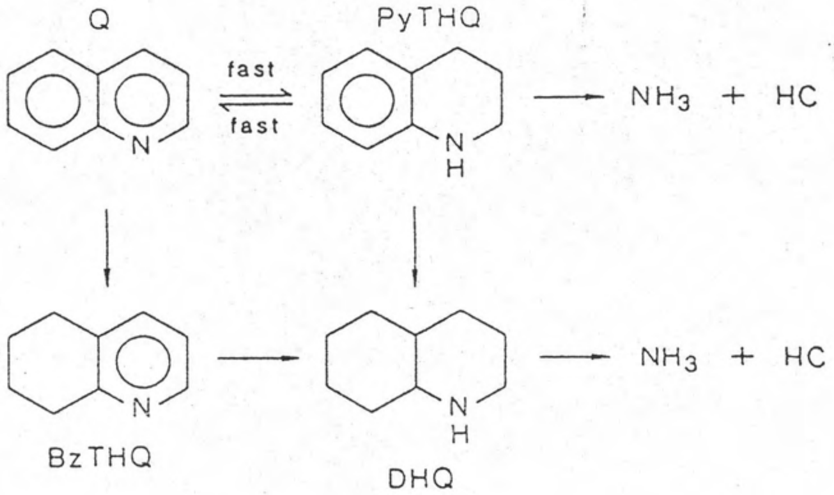

Figure 2.6 Reaction Network of Quinoline
Proposed by Gultekin et al. (90)

Table 2.10 Effects of H_2S, H_2O, and NH_3 on Reaction Rate Constants ($R_i = k_i/k_{iQ}$)*

	Feed				
	Q	$Q+H_2S+H_2O+NH_3$	$Q+2H_2S+H_2O+NH_3$	$Q+H_2S+2H_2O+NH_3$	$Q+H_2S+H_2O+2NH_3$
R_1	1.00	1.42	2.33	1.13	0.33
R_2	1.00	0.90	0.80	0.99	1.03
R_3	1.00	1.00	0.80	1.06	1.06
R_4	1.00	0.80	0.67	0.89	0.98
R_5	1.00	1.38	1.33	1.13	1.14
R_6	1.00	1.14	1.15	1.05	1.03

* From Gultekin et al. (90)

groups: (1) sintering or thermal deactivation, (2) fouling, and (3) poisoning (2, 13).

2.5.1 Sintering is an irreversible physical process leading to loss of area of the catalyst. It can occur when the catalyst is operated above the normal temperature range. Temperature rises may be localized at the individual areas where reaction occurs or may occur throughout the catalyst. Sintering can be classified into 2 kinds: one occurs due to loss of specific area which cause changes in the pore structure. A second type, where the active metal ingredient supported on a high area oxide support, sintering may occur by agglomeration or decreased dispersion of the metal crystallites on a supported metal catalyst (2)

2.5.2 Fouling or coking may be either physical or chemical process in nature but is genarally used to describe a physical blockage such as the carbonaceous deposits, coke, (42) or the deposition of metal sulfide from the organometallics in petroleum which react with sulfur-containing molecules and deposit within the pores of the catalyst during operations (43). Coke deposition also occur if reaction occurs. It cannot be eliminated by purification of the feed or use of a guard catalyst but it can be minimized by modification of the catalyst or by appropriate choice of reactor and operating conditions (2). Ocampo et al.(42) studied the HDS catalyst deactivation due to carbonaceous deposits. They found that the deactivation of the catalysts occurs within the first few hours of coal processing. It was a nonpermanent deactivation caused by the deposition of carbonaceous materials in the pores of the catalyst.

2.5.3 Poisoning is catalyst deactivation due to the adsorption of some impurity in the feed stream or to the adsorption of a product of the reaction onto the active sites of the catalyst. The most usual type of this process is caused by an impurity in the feed stream. The poisoning may either be temporary or permanent. The former implies that the poison is not adsorbed too strongly and catalyst activity may be restored by eliminating the source of the poison from the feed stream. Permanent poisoning is an irreversible process because the poison is adsorbed too strongly. It is a major problem, so the catalyst has to be discharged ultimately (13). The poisoning deactivation by trace metal impurities, such as Ni, V, Pb, As, Hg, Fe, and Ti etc., can permanently deposit on the active sites of the catalyst and cause a loss of catalytic activity. Katzer et al.(44) reported that samples of deactivated catalyst near the inlet of the reactor were 50-70 % covered with a crust of FeS which was responsible for activity reduction. They also found small amounts of Cu, Si, Al, Zn, and Ti on the catalyst but the exit of the reactor was free of FeS.

The deposition of metal impurities is considered to have a long term effect (45). In principle it is alway possible to remove impurity poisons from the feed stream and there are three ways of minimizing of the effects of poisoning on catalysts: First, purification of the feed stream. Second, using a guard reactor or a guard catalyst before the main reactor. Finally, designing of the reactor to minimize poisoning effects.

Kovach et al.(45) and Karr and McCaskill (46) reported that Na, K, Mg, Ca, P, Ti, Fe, V, Sn, Pb, Co and Si permanently poisoned catalyst at different rates and deposition of organometallics, such as those of Ti, gained access to the surfaces and adsorbed in high concentration. These metals were found as oil-soluble organometallics. The activities of the catalysts in ring cleavage quinoline were reduced by these metals. The iron deposition was limited to the outer catalyst surface (98).

Coal liquefaction catalyst characterized was studied by Thomas and Sample (47) and Thakur and Thomas (48) who found that the major changes of the catalysts during the tests include 4-8 wt % contaminants metal and 17-22 wt % coke. The major metal contaminants were Ti, Fe, B, Ca, Mg, and Si. The carbonaceous residue increased rapidly and reached a steady state values in < 10 days. Coke was uniformly distributed throughout the catalyst extrudate while the metal penetration was restricted to 200-300 um of the outer surface of extrudate in both cases. All physical properties decreased with increasing coke content. Coke deposition gave a diffusivity resistance of reactant. The decline in activity was proportional to the coke and metal contents of the catalysts (49). The larger amount of metallic foulants caused more serious active-site poisoning and pore-mouth poisoning (53).

Crynes and Seapan (50) found that more than half of the catalyst activity loss and coke buildup occured during the 1st 40 hr on stream. Both hydrogenation and hydrodenitrogenation can be related to coke content. The amount of coke on spent catalysts increases sharply as the operation time increases and then level off (51). The deposition of trace metal on the catalysts surface increases linearly with the increasing operating time, but at a decreasing rate (51, 52).

For quinoline hydrodenitrogenation, Stohl (54) studied the causation of catalyst deactivation by using a NiMo/alumina as a catalyst at 300 and 400 °C for 5 and 120 minutes, respectively. They found that quinoline, 1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline, and decahydroquinoline caused most of the deactivation and gave the highest carbon deposition, while propylcyclohexane caused least deactivation and gave the lowest carbon deposition. Hisamitsu et al.(77) found that the deactivation rate of the catalyst in hydrodenitrogenation (HDN) from As deposition on catalyst was higher for shale oil than for petroleum.

Whereas, Horita and co-worker (56, 57) and Adkin et al. (58) found that the C , Na, and Mg were deposited uniformly on the catalyst. During the initial period of the run, rapid deactivation occurs as C was quickly deposited while the slow deactivation was caused mainly by deposits of Na contaminants. High H pressure prevent coke deposition while metal deposition decreased with increasing H pressure,

Fish et al.(59) found that the nickel oxide catalyst used in gas-phase hydrodenitrogenation reaction was irreversible poisoned by sulfur and slowly deactivated during HDN due to coke formation. It can be regenerated by oxidation in air and subsequent reduction in H.

2.6 Effect of Other Elements on Catalyst Activity

Many researches were carried out to investigate the effects of various elements on the catalyst activity or selectivity. The catalytic activity or selectivity in hydrodenitrogenation reaction may be suppressed or enhanced by some elements.

The effects of phosphorus on the activity and selectivity of NiMo/alumina catalysts in hydrodenitrogenation of model N-compound were studied (60, 61, 62, 63, 64). The catalysts contained with phosphorus were less susceptible to coke formation and gave a hydrogen-rich coke. Phosphorus-addition to the catalyst did not improve the hydrogenation activity and had a slight enhancement in the hydrodenitrogenation activities. However, the P-promoted catalysts had higher activity than the unpromoted catalysts. Hydrogenolysis activity was increased by P-promoted catalyst.

The conversion of quinoline to hydrocarbon over Ni and Mo catalysts had improved only slightly in the presence of phosphate (63). The addition of phosphate to NiMo/alumina and Rh/alumina catalysts increased the HDN conversion slightly and the increasing of P-loading increased the selectivity for propylbenzene (64). Whereas Song et al.(65) compared the activity of commercial boron- and phosphorus-modifided sulfided

NiMo/alumina and NiHY zeolite for hydrocracking reaction. They found that the modifided NiMo catalysts had much lower activity and conversion for this reaction than NiHY zeolite catalyst but NiHY zeolite had higher coke deposition than NiMo/alumina.

Chan et al. (66) reported the effects of titanocene dichloride on the hydrodenitrogenation of coal liquids over NiMo/alumina catalyst. They suggested that the addition of titanocene dichloride had no effect on hydrodenitrogenation or hydrogenation in the presence of glass beads at the preheating zone but it would promote these reaction in the absence of glass beads. Furthermore, Tscheikuna and Seapan (67) found that titanocene dichloride decreased Tetralin hydrogenation but had reverse effects on the mixed reactant. Coke formation on catalyst was suppressed by titanocene dichloride in Tetralin but the opposite occured in the mixed reactant. Seapan and Crynes (68) presented the final report of the investigation of titanocene dichloride under hydroprocessing condition on 2 commercial catalysts, NiMo/alumina and CoMo/alumina. This report showed that titanocene dichloride would enhance conversion and suppress catalyst coking.

The influence of titania on hydrogenation activity of cobalt/alumina catalysts was studied by Stranick et al.(69) who found that Ti-addition decreases the catalyst activity for hydrogenation reaction. This was attributed to site blocking which results from the migration of Ti species.

Many researches were carried out to studied the effects of the metallic components, such as Ni, V, Fe, Na, Mg, Ti and K, on the hydrogenation and hydrocracking activity of NiMo and CoMo catalysts (70, 71, 72, 73). These effects decreased in the following order for both catalytic activities: K > Na > Ca > Mg. The hydrogenation activity was decreased but the hydrocracking activity was increased by the deposition of V, Fe, and Ti by which these effects were decreased in the following order: V > Fe > Ti. However, Rautianien and Wei (71) found that increasing amount of Ni and V on the catalyst, CoMo/alumina, would decrease the hydrogenolysis activity, while the hydrogenation activity was increased. The hydrocracking activity was more readily lost than the hydrogenation activity by Mg-deposition on NiMo/alumina catalyst (73). The hydrogenation activity was almost completely lost depending on reaction conditions.

NiMo/alumina catalysts doped with fluoride and lithium in bitumen hydroprocessing was studied by Monnier et al.(74). This report was studied to the performance in enhancing the conversion of bitumenous oils into high quality fuels. They found that fluoride-addition to a NiMo/alumina catalyst improved hydroprocessing conversion whereas Li-addition suppressed it. Sulfer-removal was enhanced but nitrogen-removal was affected only slightly by reducing the diffusional limitations.

2.7 Literature Summary

1. The HDN reaction is a reaction between organonitrogen compounds and hydrogen, in the presence of

catalyst and under suitable optimum conditions. The reaction have two mechanisms: hydrogenation of the ring containing the nitrogen atom followed by hydrogenolysis of C-N bond occurs.

2. Hydrogenation and hydrogenolysis reaction occured on different types of active sites of NiMo/alumina catalyst.

3. Most catalysts used for the HDN reaction were NiMo/alumina catalysts.

4. The reaction network of quinoline have two pathways: one involves the formation from quinoline to PyTHQ, DHQ, and then PB and ammonia. A second pathway involves the formation from quinoline to BzTHQ, DHQ, and then PCH and ammonia.

5. The deactivation of catalyst used in HDN reaction occurred from the adsorption of coke and the deposition of metal.

6. Quinoline, PyTHQ, BzTHQ, and DHQ caused most of the deactivation and gave the highest carbon deposition, while PCH caused least deactivation and gave the lowest carbon deposition.

7. Deposition of organometallics, such as those of Ti and Fe, gained access to the surface and adsorbed in high concentration.

8. The organometallic could diffuse easily into the inner pore structure, thereby reducing a greater portion of the surface to a state of inactivity.

9. Deposited oxide titanium showed little deactivation effect on the hydrogenation activity of the catalyst.

10. The rate of iron adsorption was very rapid and had high level of adsorption on catalyst surface.

11.Adsorbed inorganic forms of titanium had no poisoning effects on the catalyst, but that organometallic forms were easily adsorbed from even low concentrations. The amount of titanium deposited increased very slowly.

12. Titanium in form of titanium prophyrin slightly decreases hydrodenitrogenation activity.

13. Titanocene dichloride had no effect on hydrodenitrogenation and decrease the formation of coke on catalyst.

14. The depositions of Fe and Ti decrease hydrogenation activity, but increase hydrocracking activity. These effects decreased in the following order: Fe > Ti.