

CHAPTER II

LITERATURE REVIEWS

2.1 Hydrodenitrogenation Mechanisms

In present commercial practice hydrodenitrogenation proceeds incidentally to catalytic hydrodesulfurization at elevated temperatures and pressures. Most experimental work on hydrodenitrogenation has been done at temperatures from 300 to 450°C (570 to 850°F) and pressures from 250 to 6,000 psig.

Model compound studies of various heterocyclic nitrogen compounds have shown that hydrodenitrogenation proceeds via saturation (hydrogenation) of the heterocyclic ring, followed by hydrogenolysis of C-N bonds first to open the heteroring and then to convert the resulting aliphatic or aromatic amine intermediates to hydrocarbons and ammonia. Under hydrodenitrogenation reaction conditions, hydrogenolysis of C-N bonds is essentially irreversible, but saturation of heterocyclic rings is potentially reversible depending on the temperature and hydrogen partial pressure. Ideally, hydrodenitrogenation should selectively hydrogenate only the heterocyclic rings, avoiding saturation of desirable aromatics and olefins and minimizing hydrogen consumption.

Postulated hydrodenitrogenation mechanisms of representative heterocyclic nitrogen compounds are shown in Figure 2.1. Side reactions also occur (Cocchetto and Satterfield, 1976; Satterfield and Cocchetto, 1981).

2.2 Hydrodenitrogenation of Quinoline

Hydrodenitrogenation of quinoline investigated by

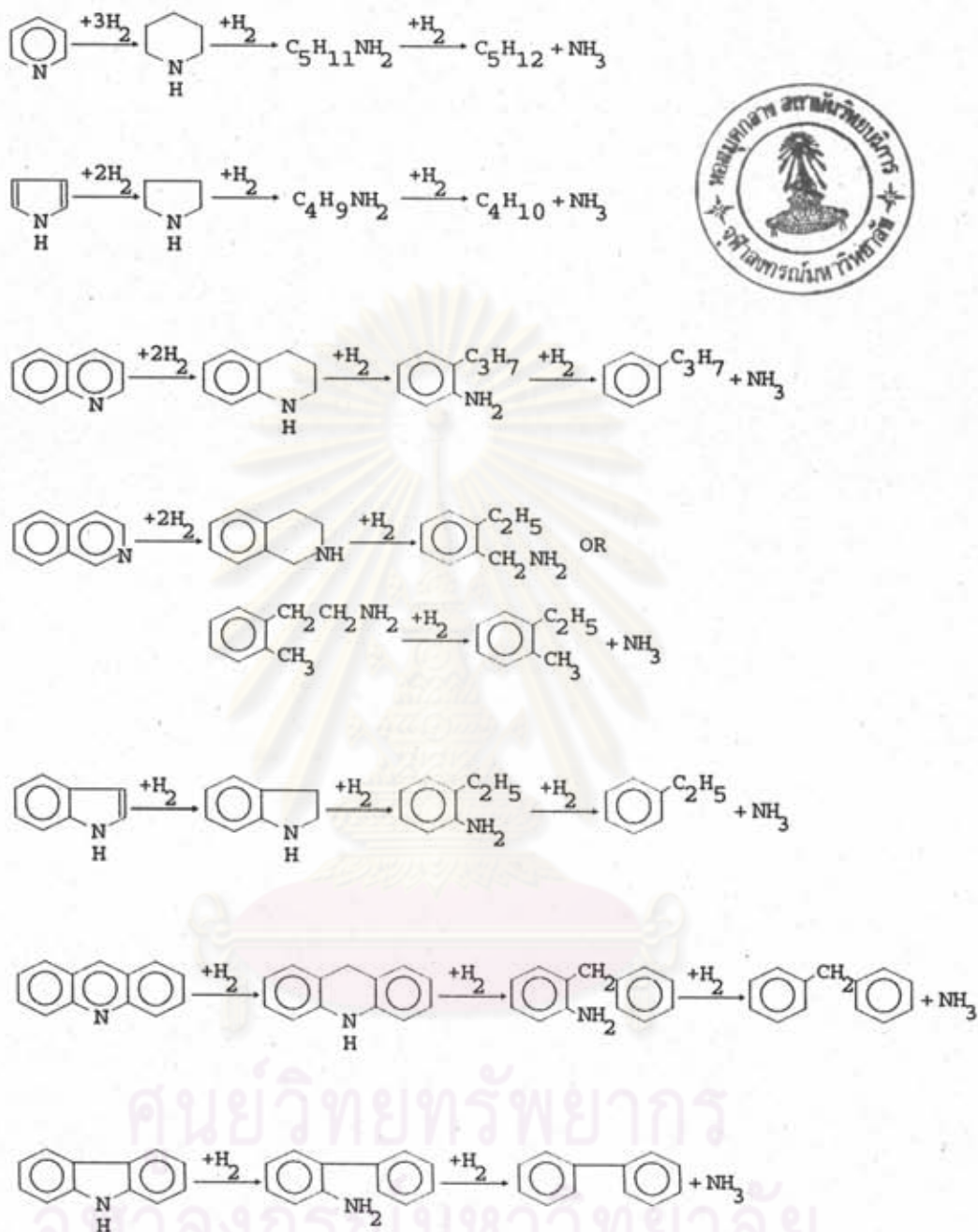


Figure 2.1 Postulated hydrodenitrogenation Mechanisms of Representative Heterocyclic Nitrogen Compounds (From Cocchetto and Satterfield, 1976)

several authors can be summarized as follows:

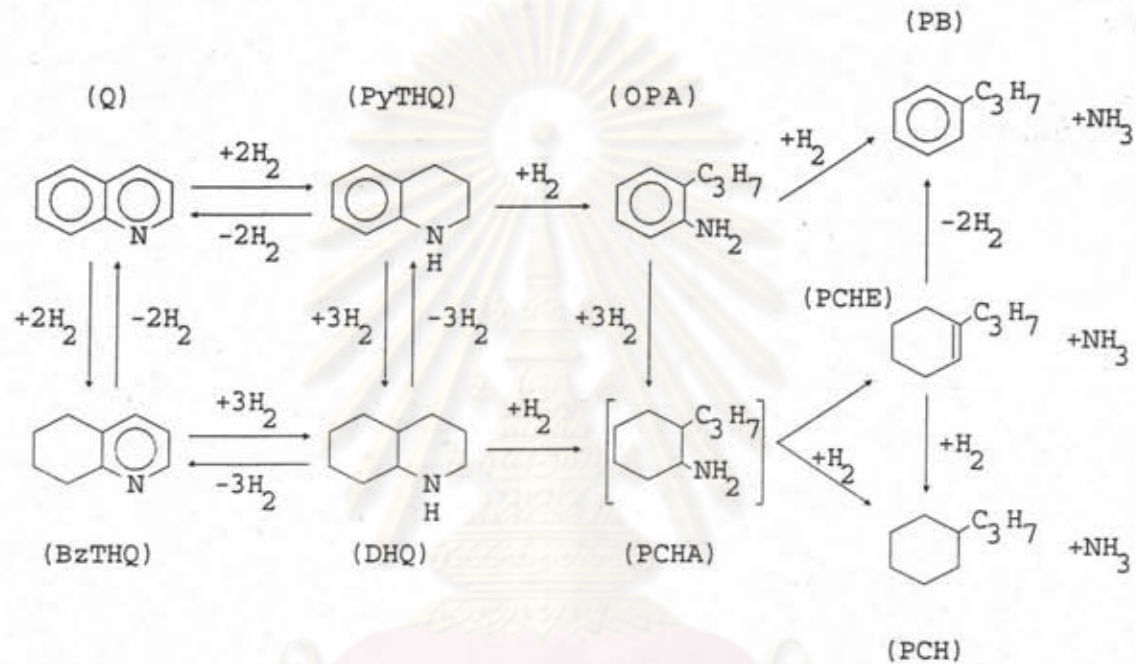
Satterfield et al. (1978) reported on the

intermediate reactions in quinoline hydrodenitrogenation, as determined in a vapor-phase microreactor packed with presulfided NiMo/Al₂O₃ catalyst at 500 psig (3.55 MPa) and 1,000 psig (7.0 MPa), temperatures of 230 to 420°C, and quinoline partial pressures of about 13 to 110 kPa. Under all conditions studied, quinoline is rapidly hydrogenated to an essentially equilibrium concentration of 1,2,3,4-tetrahydroquinoline. The dominating initial reaction pathway varies greatly with temperature. At the lower temperatures the concentration of quinoline is much less than that of 1,2,3,4-tetrahydroquinoline and the latter is then converted either to o-propylaniline or to decahydroquinoline. At the higher temperatures the equilibrium concentration of 1,2,3,4-tetrahydroquinoline is much diminished relative to quinoline, and the conversion rate of the latter to 5,6,7,8-tetrahydroquinoline and subsequently to decahydroquinoline and their products become significant. Under the more extreme conditions, a significant fraction of quinoline was converted to various high molecular weight substances including some nitrogen-containing molecules which may be difficult to react further. Shih et al. (1977) investigated the kinetics of quinoline hydrodenitrogenation in a batch liquid-phase (slurry) reactor employing a sulfided NiMo/Al₂O₃ catalyst and a paraffinic white oil carrier liquid. They observed rapid equilibration between hydrodenitrogenation and 1,2,3,4-tetrahydroquinoline but the other hydrogenation reactions as well as the hydrogenolysis reactions were reported to be kinetically controlled. These reaction rates were each modelled by first-order kinetics, and the corresponding rate constants were determined by a computer fitting technique. It was concluded from the kinetic analysis that nitrogen removal occurred primarily through the 5,6,7,8-tetrahydroquinoline and decahydroquinoline intermediates.

Cocchetto and Satterfield (1981) investigated chemical equilibria among quinoline and its reaction products in hydrodenitrogenation and proposed the steps believed to be significant in its overall hydrodenitrogenation reaction network were presented in Figure 2.2.

Satterfield and Cocchetto (1981) reported a study of the reaction network and kinetics of the vapor-phase catalytic hydrodenitrogenation of quinoline. Studies were made in a continuous flow, fixed-bed catalytic reactor system at 3.55 MPa (515.0 psig) and 7.0 MPa (1,015.5 psig), 330 to 420°C, and over a range of contact times, on a presulfided commercial NiMo/Al₂O₃ hydrotreating catalyst. In all cases the predominant hydrocarbon product was propylcyclohexane. All reactions among quinoline and its hydrogenated heterocyclic derivatives were found to be reversible. Quinoline reaches an equilibrium with respect to 1,2,3,4-tetrahydroquinoline rapidly in the presence of a NiMo/Al₂O₃ catalyst but with longer contact times the ratio 1,2,3,4-tetrahydroquinoline/quinoline can decrease below the equilibrium value, due to the much greater adsorptivity of 1,2,3,4-tetrahydroquinoline which reduces access of quinoline to the catalyst.

Satterfield and Yang (1984) studied catalytic hydrodenitrogenation of quinoline in a trickle-bed reactor and compared with vapor phase reaction over a commercial NiMo/Al₂O₃ catalyst at 350, 375, and 390°C and 6.9 MPa (1,001.0 psig) using quinoline or various intermediate reaction products. They found that the reaction rate constants for the various hydrodenitrogenation reactions in the presence of an inert paraffin liquid are very similar to those for the same reactions in the vapor phase, although the liquid tends to equalize the adsorptivities of the various nitrogen compounds present. Over a wide range, for a



Q	quinoline	OPA	o-propylaniline
PyTHQ	Py(or 1,2,3,4)-tetrahydroquinoline	PCHA	propylcyclohexylamine
BzTHQ	Bz(or 5,6,7,8)-tetrahydroquinoline	PB	propylbenzene
DHQ	decahydroquinoline(cis and trans isomers)	PCHE	propylcyclohexene
		PCH	propylcyclohexane

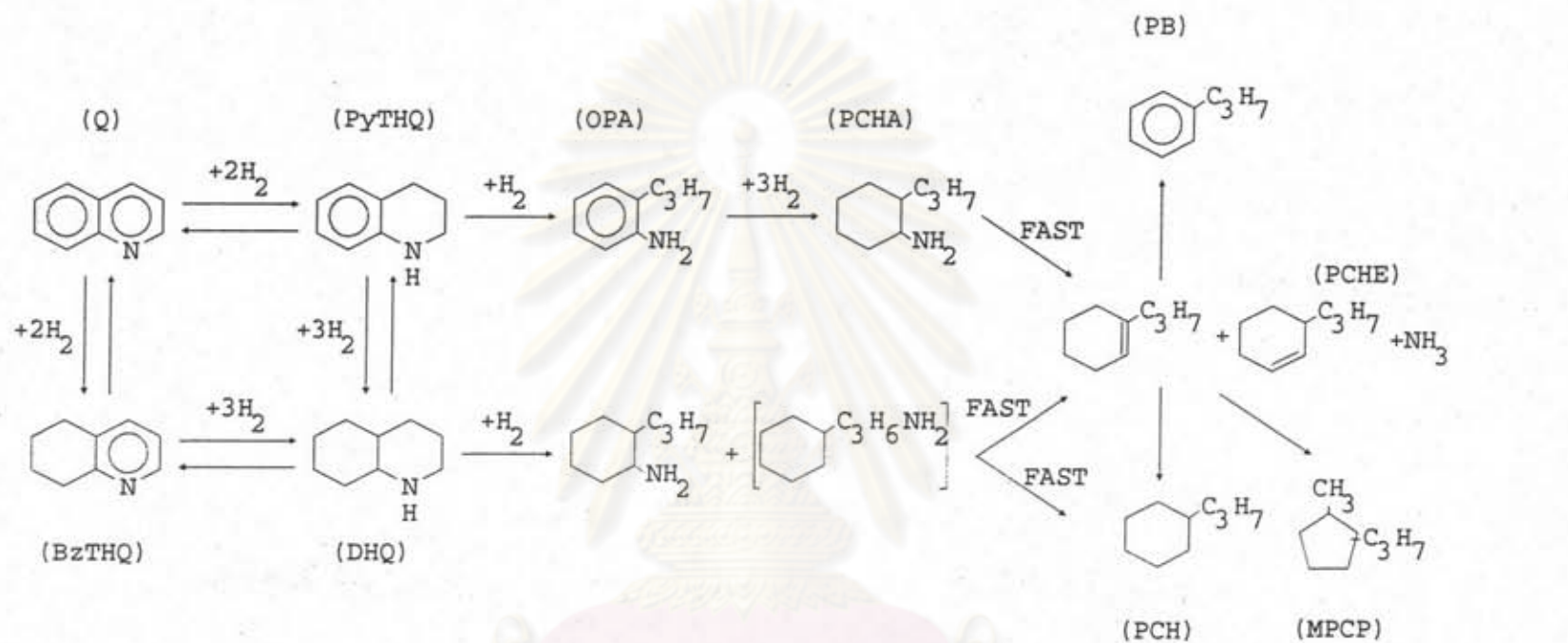
Figure 2.2 Quinoline Hydrodenitrogenation Reaction Network (From Cocchetto and Satterfield, 1981)

specified pressure and temperature, the percent conversion as a function of contact time is remarkably similar for liquid- and vapor-phase processing. In both cases, the overall hydrodenitrogenation reaction is essentially zero order under the conditions studied. Equilibrium between quinoline and 1,2,3,4-tetrahydroquinoline is rapidly attained in both vapor-phase and liquid-phase processing. A tentative revised reaction network for quinoline hydrodenitrogenation based on previous and new information is shown in Figure 2.3. They also reported that the heavier products are formed in the greatest amount at the highest temperature and slowest flow rates. Table 2.1 shows side products from quinoline hydrodenitrogenation reaction.

Gloa and Lee (1986) studied the effect of hydrogen pressure on catalytic hydrodenitrogenation of quinoline. The experiments were conducted in a stirred batch reactor at constant temperature ($T = 350^{\circ}\text{C}$) and in the presence of a presulfided catalyst ($\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst). The hydrogen pressure, kept constant during each run, was varied in the range 10.5 bar (152.3 psig) to 151.6 bar (2,199.3 psig). The experimental results showed that a necessary condition for the elimination of the nitrogen atom is that hydrogenation of the rings containing this element be completed first. The effect of hydrogen pressure on reaction network for quinoline hydrodenitrogenation is depicted in Figure 2.4.

2.3 Hydrodenitrogenation Catalyst

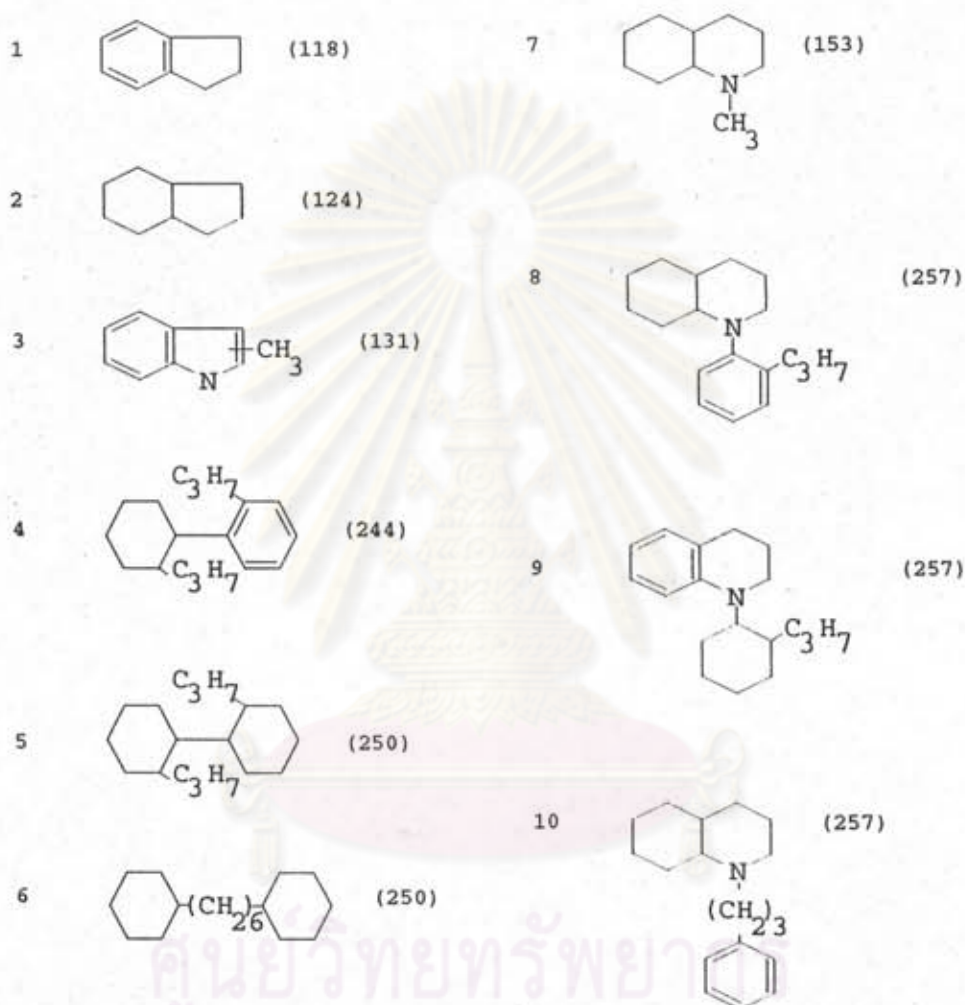
The hydrotreating of petroleum fractions for the removal of sulfur and nitrogen is considerable importance in petroleum refining since many problems experienced in catalytic processes can be traced directly to poisoning of the catalysts by sulfur and nitrogen compounds. Catalysts developed for desulfurization are currently



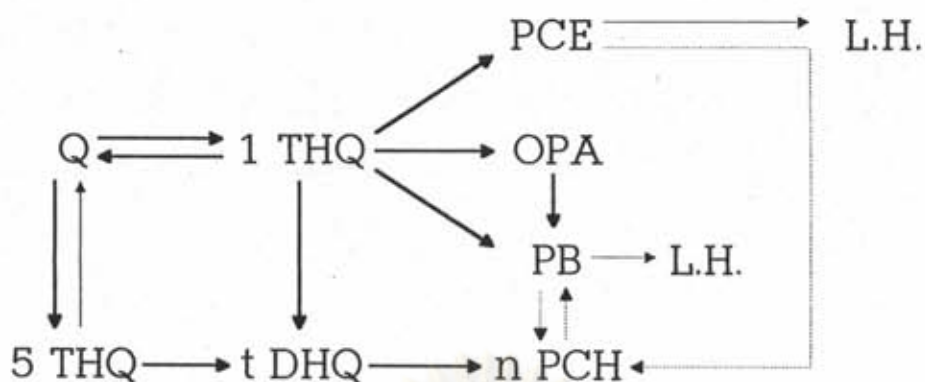
Q	quinoline	PCHA	propylcyclohexylamine
PyTHQ	Py(or 1,2,3,4)-tetrahydroquinoline	PB	propylbenzene
BzTHQ	Bz(or 5,6,7,8)-tetrahydroquinoline	PCHE	propylcyclohexene (1,1 or 1,3)
DHQ	decahydroquinoline(cis and trans isomers)	PCH	propylcyclohexane
OPA	o-propylaniline	MPCP	methylpropylcyclopentane

Figure 2.3 Revised Reaction for Quinoline Hydrodenitrogenation (From Satterfield and Yang, 1984)

Table 2.1 Side Products from Quinoline
 Hydrodenitrogenation Reaction Identified by
 GC/MS (Numbers in Parentheses are Molecular
 Weights) (From Satterfield and Yang, 1984)



being used for denitrogenation also, but higher temperatures and pressures are required to remove the nitrogen compound. Generally, the dual functional catalysts are used, the most active being sulfided cobalt or nickel molybdate, or nickel tungsten sulfide supported on silica alumina. However, the high temperatures and pressures required for the denitrogenation of heavy petroleum fractions, shale oil, and coal tar have prompted research to find more active catalysts.



——— ALL PRESSURES
 - - - - LOW PRESSURES
 HIGH PRESSURES



Q = quinoline
 1THQ = 1,2,3,4-tetrahydroquinoline
 5THQ = 5,6,7,8-tetrahydroquinoline
 OPA = o-propylaniline
 tDHQ = trans-decahydroquinoline
 PB = propylbenzene
 nPCH = normal propylcyclohexane
 PCE = propylcyclohexene
 L.H. = lighter hydrocarbon

Figure 2.4 The Effect of Hydrogen Pressure on Reaction Network for Quinoline Hydrodenitrogenation (L.H. stands for "lighter hydrocarbons") (From Glola and Lee, 1986)

McCandless and Berg (1970) investigated the hydrodenitrogenation of a heavy California gas oil using a supported NiCl_2 catalyst while methylene chloride was used to maintain a high HCl partial pressure in the reactor and keep the metal in the chloride form. The study was carried out in a continuous flow system and the

process parameters were established for maximum denitrogenation. Under identical operating conditions the system was more active for nitrogen removal than commercially available nickel tungsten sulfide and cobalt molybdate hydrotreating catalysts but, contrary to experience with the conventional catalyst, the sulfur removal was at a relatively level. Using this catalyst system the nitrogen accumulates at the cool reactor outlet combined as NH_4Cl . The high denitrogenation activity may result from an interaction between the acid catalyst system and the basic nitrogen compounds.

Zeolites are finding new application in catalysis because of their definite pore size, shape-selective nature and their high acidity. Akgerman and Sanghvi (1984) investigated quinoline denitrogenation on zeolite-based catalysts. Zeolite-based catalysts ion exchanged with nickel and impregnated with molybdenum were prepared. The kinetics of total nitrogen removal were studied at 618 to 663 K (345 to 390°C) and 17 MPa (2,466 psig). They found that a zero-order model with no intercept and a first-order model with an induction period predict the nitrogen removal rate with sufficient accuracy.

Aboul-Gheit (1987) studied effect of support acidity on the intermediate steps in hydrodenitrogenation of quinoline and indole by using two catalysts containing identical metallic constituents but differing in their cracking-promoting constituents; i.e., catalyst I (3% CoO -10% $\text{MoO}_3/\text{Al}_2\text{O}_3$) was supported on gamma-alumina while catalyst II (3% CoO -10% $\text{MoO}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$) had a silica-alumina support. A stir batch autoclave was used at an optimum stirring velocity of 1,500 r.p.m.. The operating conditions employed were: temperature from 350 to 400°C, total hydrogen pressure of $2 \times 10^7 \text{ Nm}^{-2}$ (2,900 psig), reaction period up to 10 hours, and a feedstock to catalyst ratio of 10:1. In each run, 20 g of fresh

catalyst was used. The experiments indicated that silica-alumina support gives more rate constant for the overall hydrodenitrogenation than gamma-alumina support and temperature has effected on rate constant for the overall hydrodenitrogenation of quinoline hydrodenitrogenation than indole hydrodenitrogenation. This indicates that higher catalyst acidity enhances quinoline hydrodenitrogenation more significantly than indole hydrodenitrogenation. Furthermore, all rate constants for intermediate steps either quinoline or indole, except for rate constant in indole hydrogenated to indoline, are significantly higher over silica-alumina support than over gamma-alumina. The total acidity of the silica-alumina support is 2.3 times as large as that present in the gamma-alumina. Furthermore, 29% of the acidity of the silica-alumina is of the Bronsted type, while gamma alumina contains only 5.5% of this type; in addition, the Lewis acidity in silica-alumina is stronger than that present in alumina. The tool used for those acidity correlations is differential scanning calorimetry. Since all hydrotreating catalysts are characterized by their bifunctionality, i.e., a hydrogenation function supplied by the metallic components (oxides or sulfides) of the catalyst, and a cracking function supplied by an acidic support, and since the hydrodenitrogenation reaction includes both hydrogenation and cracking steps, it should be possible to strengthen that particular catalytic function appreciably enhances the rate determining step in order to accelerate the overall reaction of a given nitrogen compound. So, two catalysts having the same hydrogenation function but differing in their cracking functions are studied in hydrodenitrogenation of these nitrogen compounds, the catalyst possessing stronger acidity is more active in enhancing the hydrodenitrogenation of quinoline than the

hydrodenitrogenation of indole, because the rate determining step in quinoline hydrodenitrogenation is a (hydro) cracking step. Aboul-Gheit (1985) also found that catalysts possessing stronger hydrogenation activities have been much more effective in enhancing indole hydrodenitrogenation than quinoline hydrodenitrogenation because the rate determining step in indole hydrodenitrogenation is the hydrogenation step.

Hirschon et al. (1987) attempted to establish whether a sulfided commercial hydrotreating catalyst (CoMo), when doped with ruthenium, will exhibit enhanced activity and selectivity, even in the presence of added sulfur. Results showed that the addition of $\text{Ru}_3(\text{CO})_{12}$, a precursor to catalysts that cleavage C-N bonds in amine transalkylation reactions, to a commercial CoMo hydrodenitrogenation catalyst greatly enhanced the activity of the catalyst and gave a 5-fold increase in selectivity to aromatic hydrocarbon products.

Shaw (1988) studied hydrodenitrogenation of aromatic nitrogen compounds with reduced hydrogen consumption using a rhenium catalyst and found that rhenium on carbon in tetralin is effective for hydrodenitrogenation of aromatic nitrogen compounds with reduced hydrogen consumption, producing mainly aromatic rather than saturated hydrocarbons. Hydrodenitrogenation of 2-ethylaniline gave a hydrocarbon product consisting of 73% aromatic and 27% saturated hydrocarbons after 85% denitrogenation. Similar results were observed for 1,2,3,4-tetrahydroquinoline, quinoline and indole.

Harvey and Pratt (1989) tested hydrodenitrogenation activity using a series of metal-containing Y-zeolites which mixed with an equal amount of a standard Ni-Mo formulation and the resulting mixed zeolite-alumina catalyst for and concluded that a catalyst containing ruthenium is the only one to show

higher activity than the reference Ni-Mo formulation.

Catalytic hydroprocessing is used to upgrade fossil fuels ranging from light petroleum naphtha to vacuum gas oils and residua. The catalysts are typically sulfided $\text{CoO-MoO}_3/\text{gamma-Al}_2\text{O}_3$ (Co-Mo) or $\text{NiO-MoO}_3/\text{gamma-Al}_2\text{O}_3$ (Ni-Mo) which can undergo deactivation at widely different rates depending on the feed and processing conditions. A naphtha hydrodesulfurization catalyst may remain active for years whereas a residuum hydroprocessing catalyst may last only a few months. Catalyst deactivation may result from (1) chemical poisoning, as feed components adsorb on catalytic sites or react to form other strongly adsorbed species, (2) physical blockage of the catalyst surface, preventing access of reactants to the catalytic sites, or (3) physical blockage of catalyst pores (or pore mouths), preventing access of reactants to the interior pore volume. Diez et al. (1990) studied influence of coke on the hydroprocessing activity using a Ni-Mo/ $\text{gamma-Al}_2\text{O}_3$ catalyst. A commercial Ni-Mo/ Al_2O_3 hydroprocessing catalyst was deactivated with from 1 to 10 wt% coke in operation with either a light catalytic cycle oil (LCCO) or a coal residuum. Coke deposition occurred during the first 20 hr. For LCCO, the quantity and aromaticity of the coke as measured by ^{13}C MAS NMR was dependent on the reactor temperature, increasing from 1.5% carbon and 40% aromatic (sp^2 carbon) at 335°C to 3.0% carbon and 70% aromatic at 395°C . Rate constants for hydrogenation, hydrodesulfurization (HDS), and hydrodenitrogenation (HDN) were approximately 10% lower for the catalyst coked with LCCO at 335°C and 20% lower for the catalyst coked with LCCO at 395°C than for the coke-free catalyst. At higher coke levels, however (10.6 wt% C with coal residuum), about 75% of the hydrogenation and HDS activity and 95% of the hydrodenitrogenation activity were lost. From the N_2 pore size distribution, the coke

thickness was modelled and estimated to be 0.3 and 0.5 nm for 1.5 and 3.0 wt% C, respectively. The coke thickness increased to 1.1 nm at 10.5 wt% carbon. Surface analysis by X-ray photoelectron spectroscopy (XPS) indicated that the alumina support may accumulate coke more rapidly than the molybdenum and nickel sulfides. It is proposed that the loss in the catalyst activity resulted from blockage of the MoS₂ crystallite edges (active sites) by coke formed on the alumina support.

Rangwala et al. (1990) investigated influence of catalyst properties and operating conditions on hydrodenitrogenation of quinoline. Results are reported for the catalytic hydroprocessing of quinoline blended into a heavy atmospheric gas oil (HAGO) by using seven different commercial catalysts. The studies were carried out in a CSTR at temperatures of 380-420°C, pressures of 7-17.3 MPa (1,015.5-2,509.8 psig) and space velocities of 11-23 cm³/(hr.g of catalyst). The nitrogen concentrations were varied from 0.3 to 0.96 wt% and were comparable to those generally found in coal-derived liquids. Limited hydroprocessing studies were also done for a coal-derived liquid (Saarbergwerke Process Oil) using both a Ni-Mo and Ni-W catalyst. The Ni-Mo catalysts were the superior catalysts, with an optimum Ni/Mo ratio of about 0.24. The kinetic studies showed that irreversible pseudo-first-order kinetics correlates the rate data for hydrodenitrogenation of quinoline only for feed nitrogen contents below about 0.3 wt%. At higher concentrations of nitrogen in the feed, an inhibition effect due to the presence of nitrogen was observed. Data on the effect of reactor pressure on hydrodenitrogenation reaction, although limited, shows that a first-order rate behavior with pressure is applicable in the pressure range 7-17 MPa (1,015-2,466 psig). The catalyst effectiveness factor based on the first-order reaction rate model for hydrodenitrogenation

reactions was found to be about 0.8-0.9 for Ni-Mo catalysts.

Liquids derived from primary coal liquefaction and bitumen extracted from oil sands have high contents of asphaltenes and heteroatoms, which makes them unacceptable for direct use (Stiegel et al., 1983). Asphaltene is defined operationally as soluble in benzene or toluene and insoluble in hexane or pentane and usually consists of condensed polyaromatic and N-, S-, and O-containing heterocyclic compounds with high molecular weights. It is known that asphaltene molecules are mainly responsible for the catalyst deactivation during the catalytic hydroprocessing and cracking processes of petroleum heavy oils, as they greatly contribute to coke and metals deposition on catalyst surface (Ohtsuka, 1977). Therefore, a major purpose in upgrading of coal liquids and bitumen is to convert asphaltene into lighter oils with low heteroatom content. Catalytic conversion of asphaltene is an essential and critical step in hydroprocessing of coal-derived liquids, bitumen extracted from oil sands and residues from petroleum. Song et al. (1991) studied effect of catalyst pore structure using four unimodal NiMo/Al₂O₃ having different median pore diameters (MPD, 120-730^oA) for hydrocracking (425^oC, 1 hr, 4.9 MPa (710.9 psig) H₂) of the asphaltenes derived from Akabira coal (Aka-Asp) and Athabasca oil sand bitumen (Aosb-Asp). The asphaltene conversions increased with increasing catalyst MPD up to 290^oA and then remained constant or decreased up to 730^oA. Aka-Asp has a much smaller molecular size but a higher aromaticity than Aosb-Asp, whereas conversion of the former appeared to be more sensitive to pore size. Higher oil yields were obtained with large-pore catalysts, while the highest oil yield from Aosb-Asp was still remarkably lower than that from Aka-Asp. Maximum hydrodeoxygenation activity appeared at an MPD of 150^oA

for runs of both asphaltenes while an MPD of 290^oA corresponded to the highest activity for hydrodesulfurization of the sulfur-rich Aosb-Asp.

Diaz-Real et al. (1993) studied hydrotreatment of Athabasca bitumen derived heavy gas oil containing 4.08% S and 0.49% N in a trickle bed reactor over Ni-W, Ni-Mo and Co-Mo catalysts supported on zeolite-alumina-silica at 623-698 K (350-425^oC), LHSV of 1-4, gas flow rate of 890 m³ H₂/m³ oil, and pressure of 6.89 MPa (999.56 psig). Results of zeolite-alumina-silica-supported catalysts are compared to those obtained with commercially available Ni-W, Ni-Mo, and Co-Mo on gamma-alumina. Ni-Mo supported on zeolite-alumina-silica was most active and could remove as much as 99% S and 89% N present in the oil at 698 K (425^oC). Furthermore, the metal loading of the catalysts on the zeolite support is about one-fourth of that required in the case of commercial catalysts.

Ho (1993) evaluated a denitrogenation-selective FeMo sulfide against a commercial desulfurization-selective CoMo catalyst to understand better the effects of catalyst selectivity for heteroatom removal on aromatics hydrogenation. The experiments were done in an upflow fixed-bed reactor with an uncracked gas oil. The FeMo catalyst, despite its low desulfurization activity, shows a higher volumetric activity for total aromatics reduction than the conventional CoMo catalyst of much higher surface area. The bulk FeMo sulfide is a good hydrodearomatization catalyst because of its high hydrodenitrogenation selectivity and activity. However, the downside to this property is that the active sites on FeMo have such a strong affinity for nitrogen compounds that significant hydrodearomatization does not occur until the bulk of nitrogen compounds is removed. On the other hand, the supported CoMo catalyst has hydrodesulfurization as its primary reaction. Its active sites appear to have less of an ability to discriminate

the nitrogen and aromatic compounds.

2.4 Effects of Sulfur Compounds on the Hydrodenitrogenation Reaction

Under industrial conditions organosulfur compounds are invariably present together with the organonitrogen compounds and the former are converted by hydrodesulfurization reactions (HDS). Furthermore, since hydrodesulfurization is easier than hydrodenitrogenation, when the reaction mixture reaches hydrodenitrogenation conditions (more severe conditions than for hydrodesulfurization), there will be a substantial amount of hydrogen sulfide (the final product of hydrodesulfurization) during the hydrodenitrogenation reactions. Therefore, mutual interaction studies among these reactions has a paramount importance. Studies have been performed determining the effects of sulfur compounds on the hydrodenitrogenation reaction can be described as follows:

Goudriaan et al. (1973) investigated the effect of hydrogen sulfide on the hydrodenitrogenation of pyridine. Pyridine was hydrogenated over a CoMo/Al₂O₃ catalyst at about 80 atmospheres pressure (1,175 psig) and at temperatures of 250-400°C. They found that at 350°C and a hydrogen sulfide pressure of 2 atmospheres (29 psig), denitrogenation was complete. At 300°C the maximum amount of nitrogen removed was 35%, the hydrogen sulfide pressure required being 10 atmospheres (147 psig). Besides, the pyridine ring hydrogenation activity of the sulfidic catalyst is greater than that of the oxidic catalyst and the presence of hydrogen sulfide has a beneficial effect on the hydrocracking activity of the catalyst.

Satterfield et al. (1975) studied interactions between catalytic hydrodesulfurization of thiophene and hydrodenitrogenation of pyridine. They reported that

pyridine hydrodenitrogenation is more difficult than thiophene hydrodesulfurization, and there is a thermodynamic limitation on the first step of the hydrodenitrogenation reaction mechanism which occurs, for example, at 5 to 11 bars (72 to 159 psig), at temperatures above about 350°C. Pyridine inhibits the hydrodesulfurization reaction as previously reported, but sulfur compounds have a dual effect on hydrodenitrogenation. At low temperatures, thiophene inhibits the reaction by competing with pyridine for hydrogenation sites on the catalyst. This retards the hydrogenation of pyridine to piperidine, reducing the overall reaction rate. At high temperatures the dominant effect is interaction of hydrogen sulfide, an hydrodesulfurization reaction product, with the catalyst to improve its hydrogenolysis (hydrocracking) activity. This increases the rate of piperidine hydrogenolysis which is rate determining at the latter conditions and enhances the overall rate of hydrodenitrogenation.

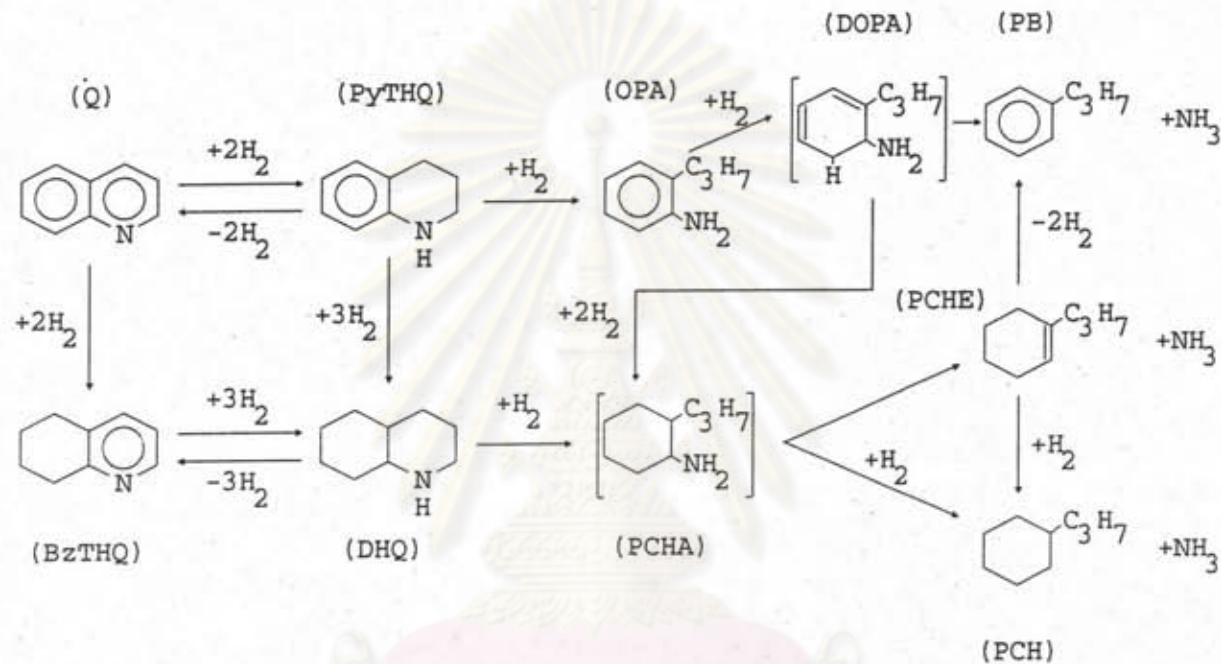
Bhinde (1979) determined pseudo-first-order rate constants for the quinoline network from data for feeds containing either 0.5 wt% quinoline or 0.5 wt% quinoline and 0.7 wt% dibenzothiophene. The rate constants for the overall nitrogen removal and for the individual reactions in the quinoline network were almost unchanged by the addition of dibenzothiophene. The only discernible effect of the dibenzothiophene was a 25% enhancement in the pseudo-first-order rate constant for the hydrogenolysis of decahydroquinoline.

Satterfield et al. (1980) investigated simultaneous catalytic hydrodenitrogenation of pyridine and hydrodesulfurization of thiophene. Studies were made with a commercial NiMo/Al₂O₃ catalyst at thiophene and pyridine partial pressures of 12.4 kPa (1.8 psig) each, total pressure of 1.14 MPa (165.38 psig), 3.55 MPa (515.01 psig), or 7.0 MPa (1,015.52 psig), and

temperatures of 200 to 400°C. It was found that under some reaction conditions thiophene enhances the overall hydrodenitrogenation of pyridine and this is caused by the H₂S formed by the hydrodesulfurization of thiophene. In the case of pyridine, the first intermediate product formed is piperidine, and the presence of thiophene caused inhibition of pyridine hydrogenation but enhancement of the hydrogenolysis of piperidine, so the net effect can be enhancement of the overall nitrogen removal rate.

Satterfield and Gultekin (1981) studied the effect of hydrogen sulfide on the catalytic hydrodenitrogenation of quinoline and reported that the presence of H₂S (from CS₂) has a slight inhibiting effect on the intermediate hydrogenation steps involved in the overall hydrodenitrogenation of quinoline but a marked accelerating effect on the intermediate hydrogenolysis steps. The net effect is an increase in the overall hydrodenitrogenation rate. The accelerating effect of H₂S on the hydrodenitrogenation rate reached a plateau value under the reaction conditions studied when the H₂S partial pressure was increased to a value corresponding to about a 1:1 mole ratio with the quinoline fed. They also proposed that on a commercial NiMo/Al₂O₃ catalyst a primary limiting factor on the overall hydrodenitrogenation rate is the very strong adsorption onto the catalyst of secondary amines formed as reaction intermediates. The steps believed to be significant in the reaction network in the presence of H₂S are shown in Figure 2.5.

They studied the hydrogenation of propylbenzene to propylcyclohexane in the presence of H₂S, or of propylamine (PA) as well and reported that H₂S or propylamine inhibit the hydrogenation of propylbenzene to propylcyclohexane but the hydrodenitrogenation of quinoline results in a higher ratio of propylcyclohexane.



Q	quinoline	PCHA	propylcyclohexylamine
PyTHQ	Py(or 1,2,3,4)-tetrahydroquinoline	PB	propylbenzene
BzTHQ	Bz(or 5,6,7,8)-tetrahydroquinoline	PCHE	propylcyclohexene
DHQ	decahydroquinoline(cis and trans isomers)	PCH	propylcyclohexane
OPA	o-propylaniline	DOPA	dihydro o-propylaniline

Figure 2.5 Quinoline Hydrodenitrogenation Reaction Network in Presence of Hydrogen Sulfide (From Satterfield and Gultekin, 1981)

to propylbenzene in the presence of H_2S than in its absence. It is suggested that dihydro o-propylaniline may be formed as an intermediate in the sequence of reactions proceeding from o-propylaniline to final hydrocarbon products.

Yang and Satterfield (1984) studied the effect of hydrogen sulfide on catalytic hydrodenitrogenation of quinoline in a trickle-bed reactor. Studies at 350, 375, and 390°C and 6.9 MPa (1,001.0 psig) showed that the presence of hydrogen sulfide (generated in situ from CS_2 added to the feed) in the overall reaction network somewhat inhibits hydrogenation and dehydrogenation reactions but markedly accelerates hydrogenolysis reactions, for a net increase in the overall rate of hydrodenitrogenation. These effects are similar to those observed previously in vapor-phase reactions. Hydrogen sulfide has little effect on the activation energies for the hydrogenation and dehydrogenation reactions but it significantly reduces those for the hydrogenolysis reactions. Certain plugging problems encountered upon reacting 5,6,7,8-tetrahydroquinoline are attributed to formation of a trimer imine as an intermediate. They also postulate the existence of two kinds of catalytic sites to explain their results: site I is a sulfur vacancy associated with the molybdenum atom while site II is a Bronsted acid site, either from an added promoter (e.g., phosphate) or from the dissociation of H_2S . Sulfur vacancies are responsible for hydrogenation and hydrogenolysis reactions while Bronsted acid sites are responsible for hydrogenolysis and ring isomerization. Adsorption and dissociation of an H_2S molecule can convert a sulfur vacancy to a Bronsted acid site plus a sulfhydryl (SH) group, as shown in Figure 2.6, but the adsorption is readily reversible if H_2S is removed from the reaction system.

Satterfield et al. (1985) studied the effect of

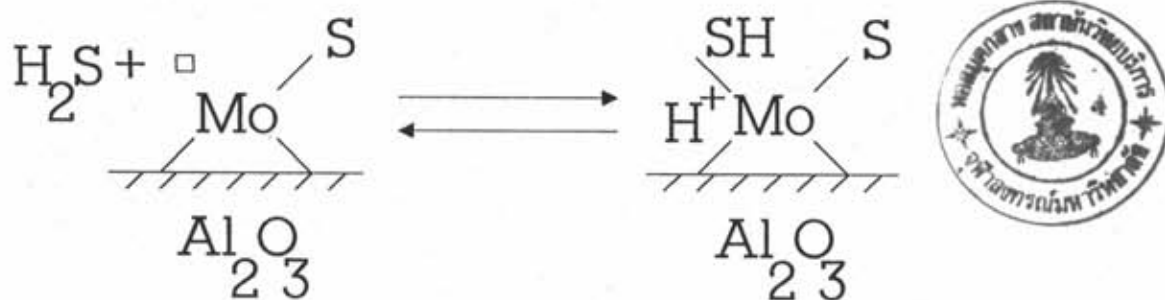


Figure 2.6 Postulated Interaction of H_2S with Catalyst
(From Yang and Satterfield, 1984)

water and hydrogen sulfide on catalytic hydrodenitrogenation of quinoline at 375°C and 6.9 MPa (1,001.0 psig). They found that the presence of water, either added as such or generated in situ from an oxygenated compound, increases the rate of hydrodenitrogenation on a $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst. The effect occurs in either the presence of or absence of H_2S (from CS_2). The degree of reversibility of this activity when water is removed varies with conditions. Any remaining enhancement is removed by a standard heating and resulfiding procedure that reduces the catalyst activity to the level it had before addition of water.

Nagai et al. (1986) investigated the selectivity of a $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst in hydrodenitrogenation, hydrodesulfurization, and hydrodeoxygenation based on the retarding effect of sulfur and oxygen compounds on acridine hydrodenitrogenation. The experiments were done in a continuous flow microreactor at $280\text{--}380^\circ\text{C}$ and 10.1 MPa (1,465.2 psig) total pressure. Sulfidation of the reduced catalyst hindered the denitrogenation of perhydroacridine to dicyclohexylmethane. The sulfur compounds which used in experiments were carbon disulfide, dibenzothiophene, benzothiophene, thiophene, dimethyl sulfide, ethanethiol. The oxygen compound was xanthene. The sulfur and oxygen compounds, except for a

small amount of CS_2 , depressed the denitrogenation at higher temperatures where the intermediate hydrogenations of acridine to perhydroacridine attained equilibria. At lower temperatures, all the additives affected the hydrogenation of octahydroacridine to perhydroacridine which was not at equilibrium and resulted in a decrease of denitrogenation.

Gultekin et al. (1989) studied the combined effects of hydrogen sulfide, water, and ammonia on liquid-phase hydrodenitrogenation of quinoline in a batch slurry reactor using presulfide commercial $\text{NiMo/Al}_2\text{O}_3$ catalyst, at 7.0 MPa (1,015.5 psig) and 330, 350, and 370°C. The kinetics of the overall hydrodenitrogenation of quinoline were found to be 0.8 order with respect to total nitrogen concentration, whereas individual rates were first order. The presence of H_2S (from CS_2) alone enhanced the overall hydrodenitrogenation rate significantly. H_2O , as such, enhanced the overall hydrodenitrogenation to some extent; however, the effect of H_2S was dominant when H_2S and H_2O were together. NH_3 (from diaminoethane) alone did not show any effect. No effect on the hydrodenitrogenation of quinoline was found in the presence of H_2S and NH_3 together. The combined effects of H_2S , H_2O , and NH_3 have resulted in a decrease in hydrogenation steps, but an enhancement in hydrogenolysis steps. The net effect was an increase in the overall hydrodenitrogenation rate.

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