CHAPTER I

INTRODUCTION

Petroleum consists predominantly of various hydrocarbons and also contains small quantities of sulfur, nitrogen, and oxygen in the form of organic compounds. Small quantities of vanadium and nickel are also present, mostly in the form of porphyrins and related structures. Elemental sulfur is also found in small quantities in some crude oils. The distribution of types of compounds and of molecular weights varies greatly with location and particular formation (depth) from which the crude oil is obtained. The most important impurities in petroleum from the point of view of catalytic processing of distillate fractions are sulfur and nitrogen compounds.

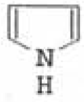
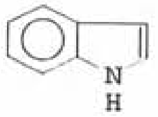
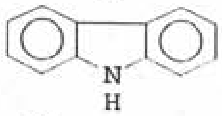
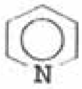
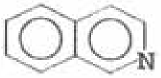
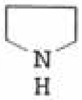
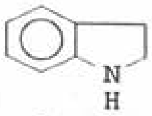
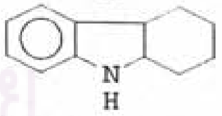
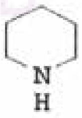
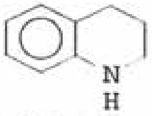
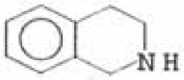
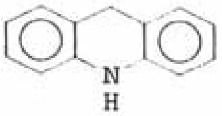
Sulfur is found in all crudes in concentrations ranging from trace to 8.0%, with most crudes in the 0.5 to 1.5% range. Sulfur is present in a wide range of aliphatic and aromatic compounds and also as elemental sulfur, hydrogen sulfide, and carbonyl sulfide (COS). The sulfur content (expressed as a weight fraction) increases with overall molecular weight, so a residual fraction would have a considerably higher sulfur content than the crude from which it is derived. In the low-boiling fractions, the principal sulfur compounds are organic sulfides or disulfides, mercaptans (thiols; R-S-H, in which R is an aliphatic group or a saturated cyclic ring), and thiophenes. In higher-boiling fractions sulfur is present largely in the form of thiophene derivatives such as benzo- and dibenzothiophenes.

Nitrogen is present in most crude oils. Its concentration is usually less than 0.2%, though it may be as high as 1.6% in some crudes. The nitrogen content increases with molecular weight of the crude oil fraction. Structures of various nitrogen compounds have not been as well characterized as those of sulfur compounds. Those compounds identified appear to be mostly heterocyclic and they are incorporated in five- or six-membered rings, most of them are unsaturated. Some representative compounds are shown in Table 1.1. These compounds can be either basic or nonbasic. Pyridines, quinolines, acridines and saturated heterocyclic ring compounds (indoline, hexahydrocarbazole) are generally basic, while pyrroles and indoles tend to be nonbasic (Cocchetto and Satterfield, 1976; Satterfield, 1980; Kirk-Othmer, 1983).

Sulfur and nitrogen compounds are undesirable, because fuels derived from them, upon burning, produce SO_2 and NO_x, which are severe air pollutants. Moreover, they are catalyst poisons in further processing steps. Nitrogen compounds, due to their basic character, preferentially adsorb on active sites of acidic catalysts used for cracking, reforming, and isomerization and hence reduce the activity of the catalyst. (Gultekin et al., 1989; Satterfield et al., 1978).

The removal of undesirable nitrogen compounds from petroleum is best achieved by catalytic hydrodenitrogenation (HDN). 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 (Satterfield et al., 1981). Under HDN 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 (Cocchetto

Table 1.1 Representative Heterocyclic Nitrogen Compounds (From Cocchetto and Satterfield, 1976)

Name	Formula	Structure
Pyrrole	C_4H_5N	
Indole	C_8H_7N	
Carbazole	$C_{12}H_9N$	
Pyridine	C_5H_5N	
Quinoline	C_9H_7N	
Isoquinoline	C_9H_7N	
Acridine	$C_{13}H_9N$	
Pyrrolidine	C_4H_9N	
Indoline	C_8H_9N	
Hexahydrocarbazole	$C_{12}H_{15}N$	
Piperidine	$C_5H_{11}N$	
1,2,3,4-Tetrahydroquinoline	$C_9H_{11}N$	
1,2,3,4-Tetrahydroisoquinoline	$C_9H_{11}N$	
9,10-Dihydroacridine	$C_{13}H_{11}N$	

and Satterfield, 1976).

Catalysts used in hydrodenitrogenation reaction consist of transition metal group VIII, Ni or Co, as promoter metals and group VIB, Mo or W, as active denitrogenation component. These metals are impregnated on the support such as alumina, active carbon or silica. They are usually a bifuntional catalysts having the proper balance of both hydrogenation and hydrogenolysis functions. The HDN catalysts must be converted to proper sulfided state before used in order to achieve the desired activity and selectivity. The most commonly used catalyst is Ni-Mo on alumina support.

A catalyst may lose its activity or its selectivity for a wide variety of reasons. The causes may be grouped loosely into: 1) poisoning; 2) fouling; 3) sintering or thermal deactivation of the catalyst; 4) solid-state reactions

A catalyst poison is an impurity present in the feed stream that reduces catalyst activity. In a complex reaction it may affect one reaction step more than another; hence the selectivity towards a desired reaction may be improved by deliberately adding a poison. It adsorbs on active sites of the catalyst, and if not adsorbed too strongly, it is gradually desorbed when the poison is eliminated from the feed stream. The phenomenon is then temporary. If adsorption is strong, the effect is permanent. The desorption may be enhanced by reaction with the fluid. Thus in a hydrogenation reaction a metallic catalyst may be poisoned by adsorption of a sulfur compound, but desorption may be enhanced by its conversion to H_2S by reaction with H_2 . If a reaction product is strongly adsorbed, the reaction may be termed self-poisoned or self-inhibited.

Fouling is a process of catalyst deactivation that may be either physical or chemical in nature. In general, much larger quantities of material are responsible for deactivation in fouling processes than in poisoning. The most typical of fouling processes is that of the carbonaceous deposit or "coke" that forms on most catalysts used in the processing of petroleum fractions or other organic chemical feedstocks. Activity can usually be restored by removal of the coke by burning.

Sintering is an irreversible physical process associated with loss of area of the catalyst which occurs when the catalyst is operated above the normal range of temperature. Such temperature rises may occur throughout the catalyst or may be localized at the individual areas where reaction occurs. Two different kinds of sintering may be distinguished depending on the type of catalyst employed. The first type of the catalyst is a normal high-area support type material, such as SiO_2 or the various forms of Al_2O_3 or a silica-alumina cracking catalyst, operation at high temperatures cause a loss of specific surface with associated changes in the pore structure, giving a corresponding loss in activity. The second type of catalyst is that where the active ingredient is usually a metal which is supported on a high-area oxide support. Examples are the nickel and platinum catalysts supported on alumina or silica. Here sintering can occur not only by reduction of the support area but by a "coalescence" or loss of dispersion of the metal crystallites. This loss of area of the active constituent of the catalyst causes a sharp drop in activity; furthermore this type of sintering may occur at temperatures below that at which the support material suffers loss of area.

Solid-state reactions are the loss of activity caused by changes in the chemical nature and/or composition of the constituents of the catalyst (Forzatti et al., 1984; Hughes, 1984; Satterfield, 1980)

In this research, effects of sulfur compounds on hydrodenitrogenation of quinoline are studied over commercial nickel-molybdenum/alumina catalyst. Sulfur compounds used in this study are carbon disulfide (CS_2), methyl disulfide ($C_2H_6S_2$), methyl sulfide (C_2H_6S), ethyl sulfide ($C_4H_{10}S$) and thiophene (C_4H_4S). Sulfur compounds are chosen to compare the effects of type and structure on hydrodenitrogenation of quinoline as follows:

1. The effect of structure is compared between ethyl sulfide (straight chain) and thiophene (cyclic).
2. The effect of number of sulfur atom is compared between methyl sulfide (1 sulfur atom) and methyl disulfide (2 sulfur atoms).
3. The effect of number of carbon atom is compared between methyl disulfide (2 carbon atoms) and carbon disulfide (1 carbon atom) and also compared between methyl sulfide (2 carbon atoms) and ethyl sulfide (4 carbon atoms).

Quinoline is chosen as the model compound for this study because it represents a type of nitrogen compound present in coal-derived materials, and a hydrodenitrogenation reaction network has been proposed for this compound (Cocchetto and Satterfield, 1981; Satterfield and Yang, 1984; Satterfield and Gultekin, 1981). Quinoline is a good model compound representative of the six-membered ring nitrogen heterocyclic compounds found in substantial concentrations in the middle distillate fraction of fuels having a high organonitrogen content such as those derived from oil shale, coal, and low-grade petroleum. Therefore, 0.5 wt% nitrogen as quinoline is chosen for this study. A knowledge of the hydrodenitrogenation reaction networks of model compounds on representative catalysts assumes some importance to guide studies of the hydrodenitrogenation of representative feedstocks since heterocyclic compounds are the most difficult to convert to hydrocarbons and ammonia in processing by hydrodenitrogenation. Quinoline has received considerable study since it contains both a heterocyclic ring and a benzene ring, so its reaction pattern is representative of the benzenoid derivatives of pyridine (Cocchetto and Satterfield, 1981; Satterfield et al., 1981).