VII. MECHANISM AND SURFACE CHEMISTRY

A. INTRODUCTION

The ultimate goal of catalysis is the design of catalytic materials with controlled activity, activity maintenance, and selectivity. This requires an understanding of the surface and bulk properties of the catalyst, as well as the intricate surface reactions which result in product formation. The latter is the subject of this section.

A detailed review of all the chemical steps which can occur for the various processes involved in the catalytic conversion of coal (see Section I) is beyond the scope of the present study. Instead, a summary of the most important and accepted mechanisms is given. Wherever possible, emphasis is placed on relating the effects of catalytic properties (e.g. surface composition, metal-support interactions, etc.) on the course of a given mechanism. This will serve as a preface to the more detailed treatment of these phenomena for actual processes as discussed in Part 3 of this study.

The present discussion is divided into six broad areas which encompass the key reactions involved in the processes discussed in Section I. These areas are:

- CO/H_2 Synthesis
- Water-Gas Shift
- Hydrodenitrogenation
- Hydrodesulfurization
- Polynuclear Aromatic Cracking
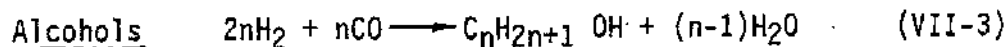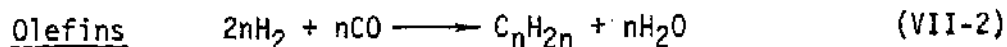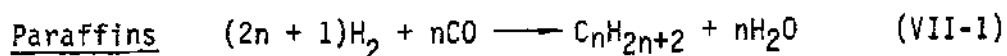- Carbon/Coal Gasification

The extent of discussion for each of these areas depends on a number of factors including the extent and quality of available information, the relevance of an area to the specific processes and problems discussed in Part 3, and the degree of need for improvement or innovation in a given area.
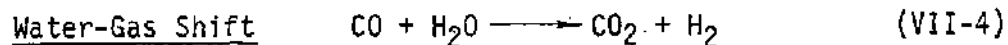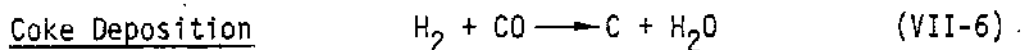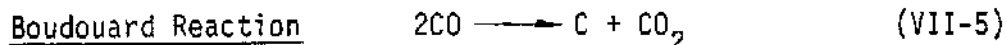
B. CO/H_2 SYNTHESIS

1. GENERAL COMMENTS

The catalytic synthesis of hydrocarbons from CO/H_2 mixtures has been known since Sabatier's work in 1902 and the more detailed developments by Fischer and Tropsch during the 1920-1935 period. Following World War II, this effort extended to the United States where a significant amount of work was carried out by a number of industrial and government laboratories. Much of this work was de-emphasized or phased out in the late 1950's because of the ready availability of petroleum. There are a number of excellent reviews which summarize this early work (1-7).

The marked increase in demand for petroleum over the last five years has generated renewed interest in the CO/H_2 synthesis area as a means of producing both fuels and chemicals. The general synthesis reactions of interest are:

Paraffins $\quad (2n + 1)H_2 + nCO \longrightarrow C_nH_{2n+2} + nH_2O \qquad$ (VII-1)

Olefins $\quad 2nH_2 + nCO \longrightarrow C_nH_{2n} + nH_2O \qquad$ (VII-2)

Alcohols $\quad 2nH_2 + nCO \longrightarrow C_nH_{2n+1} OH + (n-1)H_2O \qquad$ (VII-3)

These reactions may be accompanied by one or more of the following reactions:

Water-Gas Shift $\quad CO + H_2O \longrightarrow CO_2 + H_2 \qquad$ (VII-4)

| Boudouard Reaction | $2CO \longrightarrow C + CO_2$ | (VII-5) |
| Coke Deposition | $H_2 + CO \longrightarrow C + H_2O$ | (VII-6) |

which sometimes can lead to difficulties in a kinetic investigation.

Most of the early research in this area was done before the development of adequately sensitive analytical instruments such as gas chromatography, and therefore on-stream rapid analysis was not possible. Detailed product distributions were generally not feasible. High conversion levels were required to obtain adequate samples for analysis, and therefore few kinetic studies were conducted at differential conditions (minimum product inhibition) and at conditions which eliminate or minimize heat and mass transfer limitations. Also, most of the early work was done before the development of chemisorption techniques as a means of measuring metal surface areas. Therefore, specific activities, i.e. rates per unit surface area of metal, are not available for the early work. As shown by the recent work of Vannice (8, 9), there are significant differences in the relative activities for the Group VIII metals when measured on a specific area basis as compared to the early data reported for this group of metals. Thus, Fischer and co-workers (10) reported the following trend in decreasing activity for methanation:

Ru > Ir > Rh > Ni > Co > Os > Pt > Fe > Pd

On a specific activity basis (8), the trend becomes:

Ru > Fe > Ni > Co > Rh > Pd > Pt > Ir

As pointed out in Section III-D, one notes that iron is a very active methanation catalyst, and that the lower activity reported by Fischer was probably due to low surface area.

It is important to note, as shown by the above example, that many of
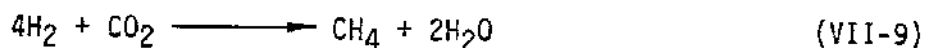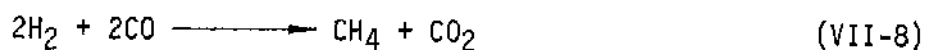
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the developments in catalysis over the last decade will play a significant role in understanding the mechanistic aspects of complex surface reactions such as those which occur during CO/H_2 synthesis. The following discussion in this area is restricted to hydrocarbon synthesis. For convenience, it is divided into two parts, methanation and liquid hydrocarbons. The former, of course, is a special case of the latter. However, because of the importance of methanation, this subdivision was felt to be warranted.

2. METHANATION

The methanation reaction is the simplest of the paraffin synthesis reactions (equation VII-1),

$$3H_2 + CO \longrightarrow CH_4 + H_2O \qquad \text{(VII-7)}$$
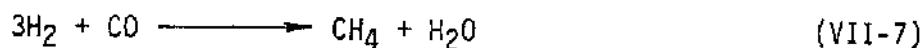
Methane is also formed by two other reactions

$$2H_2 + 2CO \longrightarrow CH_4 + CO_2 \qquad \text{(VII-8)}$$

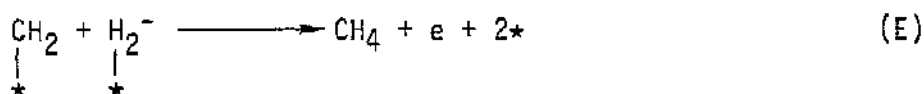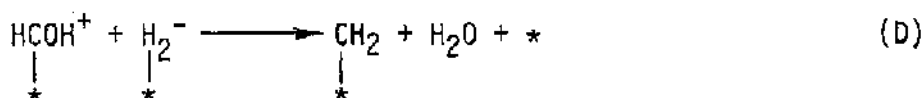$$4H_2 + CO_2 \longrightarrow CH_4 + 2H_2O \qquad \text{(VII-9)}$$

however, hydrogenation of CO_2 (VII-9) does not occur in the presence of CO (11, 12), and equation VII-8 can be considered to be a combination of equations VII-7 and VII-4. Much of the recent kinetic work in this area has been discussed in detail elsewhere (8-19). The two mechanisms which are most consistent with reported experimental data are those reported by Vlasenko and Yuzefovich (20) and by Storch, Golumbic, and Anderson (6). Both of these groups postulate the formation of an adsorbed HCOH complex in the enol form:

$$
\begin{array}{c}
H \diagdown \qquad \diagup OH \\
\diagdown C \diagup \\
\| \\
M
\end{array}
$$
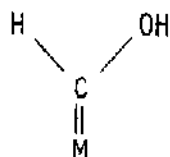
The same complex has been proposed by other workers for CO/H_2 reaction over Ru (21), Pt (22), Ni (20, 23), Co (24), and Fe (25-27), and for

all the group VIII metals (9). The Russian workers suggest the following scheme:

$$* + e + H_2 \longrightarrow \underset{\overset{|}{*}}{H_2^-} \tag{A}$$

$$* + CO \longrightarrow \underset{\overset{|}{*}}{CO^+} + e \tag{B}$$

$$\underset{\overset{|}{*}}{CO^+} + \underset{\overset{|}{*}}{H_2^-} \xrightarrow{\text{RDS}} \underset{\overset{|}{*}}{HCOH^+} + e + * \tag{C}$$
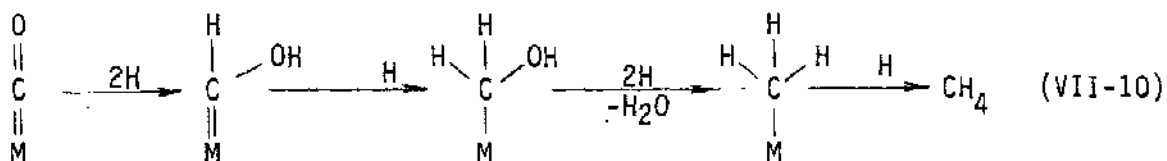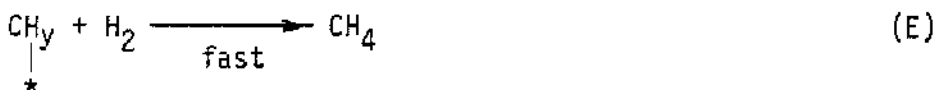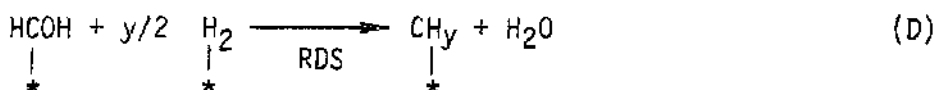
$$\underset{\overset{|}{*}}{HCOH^+} + \underset{\overset{|}{*}}{H_2^-} \longrightarrow \underset{\overset{|}{*}}{CH_2} + H_2O + * \tag{D}$$

$$\underset{\overset{|}{*}}{CH_2} + \underset{\overset{|}{*}}{H_2^-} \longrightarrow CH_4 + e + 2* \tag{E}$$
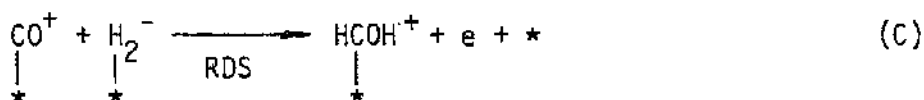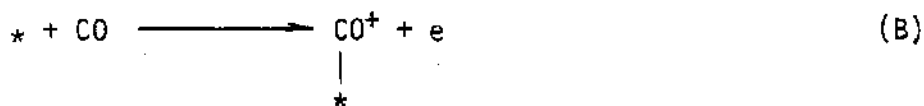
where reaction (C) is the rate-determining step. For metals which give higher molecular weight products these workers suggest that CH_2 polymerization becomes predominant (20). An alternate mechanism has been extracted (11) from the more general equations for liquids synthesis proposed by Storch, Golumbic, and Anderson (6).

$$\underset{M}{\overset{O}{\underset{\|}{\overset{\|}{C}}}} \xrightarrow{2H} \underset{M}{\overset{H}{\underset{\|}{\overset{|}{C}}}}\!\!\diagup^{OH} \xrightarrow{H} \underset{M}{\overset{H}{\underset{|}{H\diagdown\overset{|}{C}}}}\!\!\diagup^{OH} \xrightarrow[-H_2O]{2H} \underset{M}{\overset{H}{\underset{|}{H\diagdown\overset{|}{C}}}\diagdown^{H}} \xrightarrow{H} CH_4 \tag{VII-10}$$

In a very recent study Vannice has investigated the kinetics of the methanation reaction over all of the Group VIII metals except osmium (8, 9). The data were explained by a kinetic model which is similar to that proposed by the Bureau of Mine workers (6, 28) several years before.

$$CO \rightleftharpoons \underset{\overset{|}{*}}{CO} \tag{A}$$

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$$H_2 \rightleftharpoons \underset{*}{H_2} \qquad (B)$$

$$\underset{*}{CO} + \underset{*}{H_2} \rightleftharpoons \underset{*}{HCOH} + * \qquad (C)$$

$$\underset{*}{HCOH} + y/2 \underset{*}{H_2} \xrightarrow{RDS} \underset{*}{CH_y} + H_2O \qquad (D)$$

$$\underset{*}{CH_y} + H_2 \xrightarrow{fast} CH_4 \qquad (E)$$

In this work the number of H atoms, y, interacting in the rate-determining step, (D), was found to increase with increasing ability of the metal to produce higher molecular weight species. For example,

Metal	y
Pd	1
Ni	2
Co	3
Ru	4

Ru is known to exhibit a marked tendency to form high molecular weight paraffinic waxes at high pressures and low temperatures. It is reassuring to note that even though this kinetic study was carried out at atmospheric pressure, Ru was found to yield the largest C_{5+} molecular distribution. This suggests that such studies at ambient pressures and at differential conditions may distinguish between the catalytic properties of metals as they would appear at actual conditions of high conversions and pressures. Interestingly, it was also found that activity for methanation increased with H atom bond strength to the metal surface and decreased with CO bond strength to the metal. This is consistent with the kinetic model if one assumes that the bond strength

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of the metal-HCOH surface complex is directly related to the strength of the CO bond to the metal. Therefore as the latter decreases, the surface coverage of the complex is also expected to decrease and make more of the surface available for hydrogen. This tends to equalize the surface coverages of HCOH complex and H_2, and thereby increases the rate of step (D) in the mechanism (RDS). It should be noted that the existence of the postulated enol intermediate has not unambiguously been proven. However, the value of this work is the development of a reasonable kinetic model which explains data for all of the Group VIII metals.

3. LIQUID HYDROCARBONS

The formation of liquid hydrocarbons has been studied for Ru (1-11, 36-40), Fe (1-11, 29-35), and Co (1-11, 24, 41, 42) catalysts, with most of the kinetic studies concerning the latter two. As mentioned in the previous section, a kinetic model has been developed (8, 9) which is plausible and self-consistent for all of the Group VIII metals. This model is applicable primarily to the methanation reaction. However, it may be possible to generalize this model to include the production of liquids.

The overall reactions for the synthesis of paraffins, olefins, and alcohols are given by equations VII-1, VII-2, and VII-3, respectively. The currently accepted mechanism which unifies these equations involves the following sequence of surface reactions (6, 41):

(i)   Chemisorption of H_2 and CO, with CO covering most of the surface.

(ii) Interaction of chemisorbed CO with chemisorbed H_2 and/or molecular hydrogen to form an HCOH surface complex.

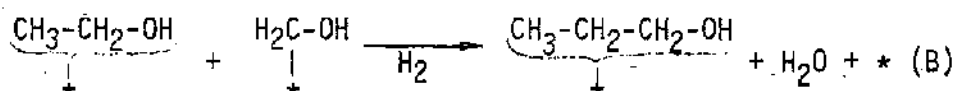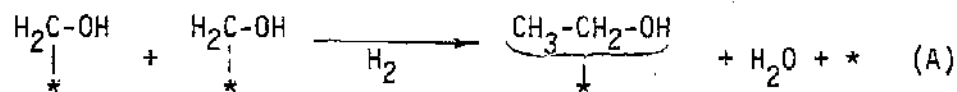(iii) Interaction of the primary HCOH complex with H_2 to form

an H_2COH complex.

(iv)   Surface polymerization to form $-CH_2$ chains with elimination of -OH as water.

(v)   Chain termination.

(vi)   Product desorption.

The presence of enolic HCOH complexes has already been discussed in the previous section. It should be noted that support for the existence of these complexes comes from early work by Weitkamp (43) which showed that alcohols are invariably found among the synthesis products, and also from tracer experiments by Kummer and co-workers (44) who found that carbon moieties of alcohols included in the CO/H_2 feed gas were found in the hydrocarbon products. This is also supported by recent work by Kölbel and Hanus (45) using short contact times and a sensitive mass spectrographic analysis of gaseous intermediates. They observed primarily HCOH at conditions where one might expect desorption of the enolic complex.

More recent work by Sastri and co-workers (24, 41, 42) shows that CO and H_2 interact on cobalt catalysts with a stoichiometry equivalent to HCOH. This work was done over the temperature range $25-100^0C$, and consisted of measuring the uptake of H_2 and CO from mixtures of the two gases. Below 50^0C these workers observed the expected competitive adsorption effects, with CO predominating as the surface species. Above this temperature, adsorption enhancement was observed until at $80-90^0C$ (42) an adsorbed H_2/CO ratio of 1/1 was observed corresponding to HCOH. At higher temperatures this species underwent facile hydrogenation to H_2COH (41). By a number of credible experiments and arguments, these workers eliminated adsorption of reactants and desorption of products as the rate-limiting step (41). This left
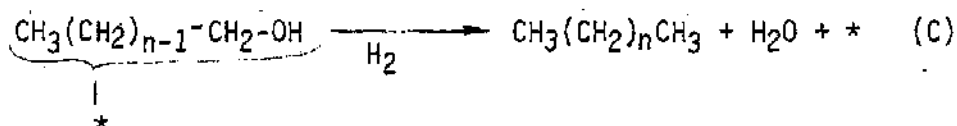
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surface polymerization of the H_2COH species and chain termination as the remaining possibilities:

Polymerization

$$H_2C\text{-}OH_{|*} + H_2C\text{-}OH_{|*} \xrightarrow{H_2} \underbrace{CH_3\text{-}CH_2\text{-}OH}_{|*} + H_2O + * \quad (A)$$

$$\underbrace{CH_3\text{-}CH_2\text{-}OH}_{|*} + H_2C\text{-}OH_{|*} \xrightarrow{H_2} \underbrace{CH_3\text{-}CH_2\text{-}CH_2\text{-}OH}_{|*} + H_2O + * \quad (B)$$

and so on.

Chain Termination

$$\underbrace{CH_3(CH_2)_{n-1}\text{-}CH_2\text{-}OH}_{|*} \xrightarrow{H_2} CH_3(CH_2)_nCH_3 + H_2O + * \quad (C)$$

Of these two processes, chain termination is expected to be the slower step, otherwise methane would be a principal product rather than higher molecular weight hydrocarbons. Since it was impossible to separate these two steps experimentally, the authors studied the hydrogenolysis of ethanol,

$$C_2H_5OH + H_2 \longrightarrow C_2H_6 + H_2O \qquad\qquad (VII\text{-}11)$$
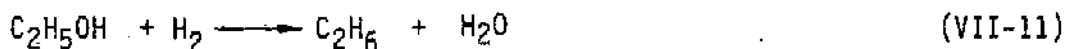
a reaction which closely models chain termination. The kinetic parameters such as activation energy were very similar to those observed for the synthesis reaction. Therefore, it was concluded that chain-termination by hydrogenolysis of the polymerized enolic surface complexes is the rate-determining step for CO/H_2 synthesis of hydrocarbons over Co catalysts. This is exactly the conclusion reached by Vannice for methanation of CO/H_2 mixtures over Group VIII metals (see equation D, last section). Therefore, this mechanism is likely to have general application for most metal catalysts.

A final point worth noting is that Fe catalysts tend to give much higher yields of CO_2 than other catalysts such as Co, Ru, or Pt.

For the latter, most of the oxygen-carrying product tends to be H_2O. For economic reasons the latter is preferable because removal of CO_2 from the product stream is more expensive than H_2O removal. As shown by Dry and co-workers (35), the formation of CO_2 over Fe catalysts is due to the high activity of these systems for the water-gas shift reaction.

4. IMPLICATIONS OF KINETIC STUDIES

Kinetic studies of CO/H_2 synthesis reactions over the past several years have established a mechanism which is credible and self-consistent. Accepting this mechanism and its implications, one can then assess the utility of various innovations in catalysis over the past decade in solving the key problem for CO/H_2 synthesis reactions to liquid hydrocarbons, namely selectivity control. Activity enhancement for methanation will not be treated here, because as discussed in Section VI and Part 3 of this study, the primary problems in this area are catalyst stability and activity maintenance in the presence of poisons such as sulfur and carbon. The same problems are, of course, found for liquids synthesis catalysts. These are discussed in Section VI.

Clearly, the bond strength of the reactants (CO, H_2) to the surface of the catalyst have been shown to significantly affect catalytic activity for the simple methanation reaction (8, 9). This is caused by two effects, alteration of the stability of the HCOH enolic complex, and changing surface concentrations of CO and H_2. Both of these phenomena should also affect product selectivity for the synthesis of liquid hydrocarbons. Indeed, there is evidence that this is the case. For example, promoters such as K_2O which are strong bases have

been used extensively to modify the activity and selectivity of synthesis catalysts (29-35). These promoters are considered to donate electrons to the surface metal atoms which in turn can strengthen the M-C bond of the adsorbed CO. This is because CO acts as an electron acceptor when it adsorbs on metal surfaces. This modification can in turn affect the reactivity of HCOH species which is formed upon hydrogenation. The selectivity of Fe catalysts is shifted toward the production of higher molecular-weight liquids when promoted with K_2O. This can be rationalized because the increased Fe-C bond strength increases CO surface coverage as well as surface residence time, and therefore there is an increase in the probability of chain growth. Hydrogen in contrast to CO behaves as an electron donor on iron surfaces, and therefore K_2O promotion results in decreased hydrogen adsorption (33). This reduces the hydrogenation activity of the catalyst which effect favors olefin formation. The latter probably forms by dehydration of an adsorbed oxygenated intermediate. These arguments are consistent with changes in heats of adsorption of CO and H_2 on K_2O-promoted iron catalysts. Promotion increases the adsorption energy of CO and decreases the adsorption energy of H_2 (33, 35). In fact, in some instances, promotion by K_2O can increase the binding energy of CO so much as to favor carbon formation (33).

In view of the above, it is useful to consider what means are available in catalysis for changing the binding energy of CO and H_2. The most promising include promotion by alkali and alkaline-earth metals, multimetallic catalysts, metal-support interactions, and crystallite size effects. These concepts have been discussed in Sections II and III, and will be applied in more detail to

CO/H_2 synthesis in Part 3 of this study. Clearly, by controlling the relative binding energies of CO and H_2, and therefore the hydrogenation activity of the catalyst, chain length can be affected. Also, if the active intermediates in chain growth are multiply bonded to the surface of the catalyst, bimetallic alloys and cluster catalysts which dilute an active metal constituent (e.g. Ni, Fe, Co, Ru) in an inert metal matrix such as Au, Cu, Ag, should affect chain length. As discussed in Section III, interruption of a uniform metal surface by decreasing particle size, or by selective poisoning would lead to the same effect.

Finally, because of the similarity of alcohol hydrogenolysis (dehydration) to the rate-limiting step in CO/H_2 synthesis, bifunctional effects brought about by changes in support acidity should be important in determining product distribution. Such effects may also be used to re-structure product molecules to other more useful products. Some work has already been done in this area which indicates that increased surface basicity substantially moderates Fe catalysts, and thereby reduces methane formation, and increases olefins and higher molecular weight species (31, 46). However, to clearly understand the nature of these and other effects will require diligent application of the catalyst preparative procedures described in Section V, and careful characterization of these catalysts both before and after use.

C. WATER-GAS SHIFT REACTION

1. SUMMARY OF KINETICS

Numerous kinetic studies have been conducted for the water-gas shift reaction:

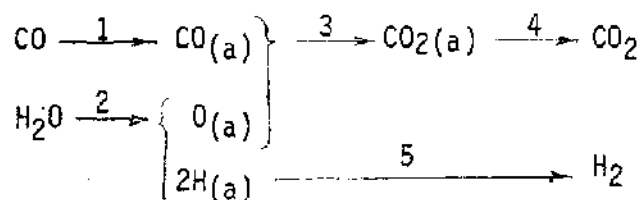$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \text{(VII-12)}$$
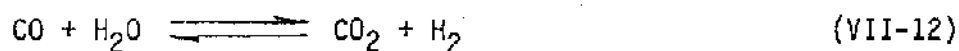
The primary interest in this reaction for the conversion of coal has been as a means to achieve the proper CO/H_2 ratio for synthesis gas prior to the methanation reaction. Most shift processes are usually run under thermodynamic equilibrium limitations. The reaction is exothermic, and therefore to minimize the CO concentration in the product stream low reaction temperatures are preferable. Indeed, the last several years have seen the evolution of low-temperature shift catalysts, usually a $CuO \cdot ZnO \cdot Al_2O_3$ complex oxide (63). These catalysts operate in the 200-250°C range compared to 350-400°C for the older Fe or $ZnO-Cr_2O_3$ catalysts. Upon reduction, the Cu catalysts consist of highly dispersed Cu ($\sim$40 $\overset{o}{A}$) stabilized with respect to thermal degradation by the presence of ZnO and Al_2O_3 (63). A primary problem with the Cu catalysts, as discussed in Part 3, is increased sensitivity to poisons such as sulfur and chlorine as compared to the high temperature catalysts. The technical challenges in this area do not lie in significant activity improvement, although this would be beneficial, but more in improving activity maintenance. In view of these facts, the mechanistic aspects of the reaction will only be discussed briefly to provide a general background for the more detailed treatment of activity maintenance in Part 3.

Many of the kinetic studies have used chromia-promoted iron oxide catalysts (47-62). In general, these studies agree that the reaction rate is:
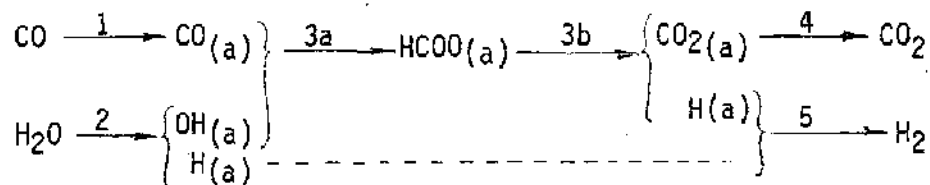
(i)   approximately proportional to CO concentration.

(ii)   retarded by CO_2

(iii)   almost independent of H_2 concentration, and

(iv)   independent of H_2O concentration when it is present in excess of stoichiometric quantities.

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Oki and co-workers (57-61) concluded from their extensive tracer work that two mechanisms are most plausible:

Mechanism I

$$CO \xrightarrow{\quad 1 \quad} CO_{(a)} \left.\begin{array}{c} \\ \\ \end{array}\right\} \xrightarrow{\quad 3 \quad} CO_2(a) \xrightarrow{\quad 4 \quad} CO_2$$

$$H_2O \xrightarrow{\quad 2 \quad} \left\{\begin{array}{c} O_{(a)} \\ \\ 2H_{(a)} \end{array}\right. \xrightarrow{\quad\quad 5 \quad\quad} H_2$$

Mechanism II

$$CO \xrightarrow{\quad 1 \quad} CO_{(a)} \left.\begin{array}{c} \\ \end{array}\right\} \xrightarrow{\quad 3a \quad} HCOO_{(a)} \xrightarrow{\quad 3b \quad} \left\{\begin{array}{c} CO_{2(a)} \\ H(a) \end{array}\right. \xrightarrow{\quad 4 \quad} CO_2$$

$$H_2O \xrightarrow{\quad 2 \quad} \left\{\begin{array}{c} OH_{(a)} \\ H_{(a)} \end{array}\right. \quad - - - - - - - - - - - - - - - \left.\begin{array}{c} \\ \end{array}\right\} \xrightarrow{\quad 5 \quad} H_2$$

The stoichiometric number approach used by these investigators led them to postulate two rate-determining steps, namely the adsorption of CO and the associative desorption of hydrogen. In the initial stages of reaction, CO adsorption is considered rate-determining, while close to equilibrium both steps become important since the value of the respective rates (steps 1 and 5) are comparable at these conditions.

2. TECHNICAL IMPLICATIONS

As in the case of CO/H_2 synthesis reactions, the interaction of CO and H_2 plays a key role in determining the rate-limiting step for the water-gas shift reaction. In view of the above mechanisms, the binding energy to the surface for both reactants should be important in this respect, especially near thermodynamic equilibrium. As previously mentioned, the binding energy of CO and H_2 to surfaces can be readily changed by a number of techniques. These include multi-metallic systems, metal-support interactions, crystallite size effects, and the use of chemical promoters. However, it is also necessary to activate (probably dissociate) H_2O, and to minimize CO_2 adsorption and

H_2 dissociation. CO_2 adsorption leads to competitive adsorption with H_2 and CO, and therefore it is effectively a poison. Facile H_2 dissociation is likely to enhance the rate of approach to equilibrium for the reverse reaction. This may be a problem because close to thermodynamic equilibrium, the rates of steps 1 and 5 are comparable, and therefore both can influence the measured rate.

Several novel water-gas shift catalysts have been developed over the past five years which approach optimization of the above mentioned parameters. For example, the Cu catalysts mentioned earlier have sufficient activity to chemisorb CO, activate H_2O, and do not readily dissociate H_2. These catalysts are therefore more active and operate at lower temperatures, thus favoring high equilibrium conversions to CO_2 and H_2. Unfortunately, the catalysts must be meticulously guarded from poisons such as sulfur and chlorine. The reasons for this, as discussed in Part 3, are that Cu has a strong affinity for sulfur, and the stabilizing ZnO constituent is readily transformed to $ZnCl_2$. The former effect gives rise to immediate poisoning, the latter to slow poisoning due to Cu crystallite growth.

Sulfur tolerant catalysts for low temperature shift conversion have been disclosed recently (64-68). These materials contain an alkali metal component such as K_2O or Cs_2O and an effective dehydrogenation function such as Re_2O_7, Re_2S_7, or $CoMoO_4$. In view of Mechanism II which postulates a formate intermediate, these catalysts are thought to operate as follows (64). The alkali metal component, in the presence of H_2O vapor, is believed to exist as a liquid phase in contact with the surface of the dehydrogenation function. The aqueous alkali metal phase then converts CO to a formate intermediate

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which is subsequently dehydrogenated to CO_2 and H_2. The interaction of these two catalytic functions apparently brings about a synergistic enhancement in catalytic activity. However, the primary advantage of such catalysts is that they may be used at low temperatures and in the presence of substantial levels of sulfur (e.g. 1 percent H_2S). They are presently effective in the 270-330°C range (64). It should be possible by the application of many of the concepts previously outlined in Sections II-VII to improve this activity and possibly the sulfur tolerance. This aspect will be discussed in detail in Part 3 of this study.

D. HYDRODENITROGENATION

1. GENERAL REMARKS

Historically, hydrodenitrogenation (HDN) has been of interest for petroleum operations because it is a means of removing basic nitrogen compounds such as pyridines, quinolines, and indoles, which can poison acidic type catalysts used in a number of refining processes (see Section VI). Due to the emerging synthetic fuels industry, there now exists a second motivating factor for nitrogen removal, namely minimizing NO_x formation during the combustion of coal or shale oil liquids. These fuels contain unacceptably higher levels of nitrogen than most petroleum crudes. However, nitrogen removal has not received nearly the attention that desulfurization has over the last decade, primarily because sulfur has been of greater concern than nitrogen in processing petroleum feedstocks. Sulfur is present at significantly higher levels than nitrogen in petroleum, and is a severe catalyst poison as well as a potential pollutant (as SO_x upon combustion).

Until recently, HDN was accomplished by the use of conventional hydrodesulfurization (HDS) technology. This required slight modifications in catalyst formulation and operation at more stringent conditions, e.g. higher temperatures and pressures and lower space velocities. The latter was necessary because HDN occurs at substantially lower rates than HDS (69-71).

With the increased incentive to develop HDN processes, research concerning the catalytic conversion of nitrogen compounds has also increased. The number of studies, while minimal, are beginning to give some insight concerning key mechanistic steps, and therefore suggest further research programs for catalyst improvements. These programs will be mentioned at the end of this section and discussed in more detail in Part 3. For the purpose of the present study, research concerning denitrogenation of model compounds has been divided into three areas, HDN of single ring heterocycles (pyridines), HDN of multi-ring heterocycles (quinolines, indoles), and the interaction of HDS and HDN reactions. As will be discussed later, the latter topic has important implications for both HDS and HDN.
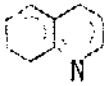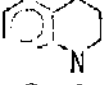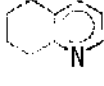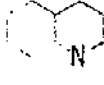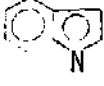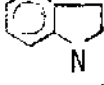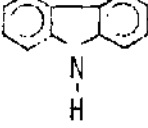
2. SINGLE RING HETEROCYCLES

Most of the work in this area has been done with pyridine. Pyrrole has seldom been used, probably because of its thermal instability. For pyridine, the mechanism of HDN has been studied by a number of workers (72-86). In general, it has been the consensus that the following sequence of reactions (78, 79)[1] takes place:

$$\text{Pyridine} \underset{2}{\overset{1(H_2)}{\rightleftharpoons}} \text{Piperidine} \underset{4}{\overset{3(H_2)}{\rightleftharpoons}} C_5H_{11}NH_2 \underset{RDS}{\overset{5(H_2)}{\longrightarrow}} C_5H_{12} + NH_3 \quad \text{(VII-13)}$$
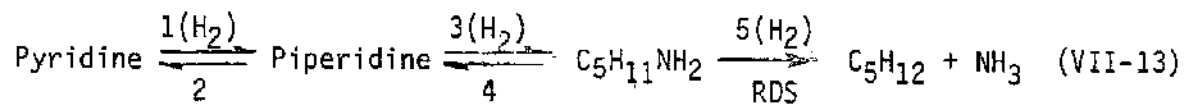
[1] For convenience, heterocycles are either named or abbreviated. The corresponding chemical formula for each is given in Table VII-1.

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TABLE VII-1

HETEROCYCLIC NITROGEN COMPOUNDS

Name	Formula
Pyrrole	
Pyrolidine	
Pyridine	
Piperidine (PIP)	
Quinoline (Q)	
1,2,3,4 Tetrahydroquinoline (THQ)	
5,6,7,8 Tetrahydroquinoline (THQ)	
Decahydroquinoline (DHQ)	
Indole	
Indolene	
Carbazole	

where C-N hydrogenolysis (Reaction 5) is considered to be the rate-determining step (RDS). Some workers have considered the RDS to be hydrogenation of the aromatic ring (80), however, most of the data at conditions of facile HDN suggest this not to be the case. Also, as recently shown by a group of Dutch workers (72-74, 76, 77), equation VII-13 is probably an over-simplification in that a number of other intermediates are detected at reaction conditions. Similar complexities are suggested by the work of other groups (80). In general, hydrogenation of pyridine to piperidine is rapid and equilibrium is quickly reached. The Dutch workers then suggest the following mechanism:

Ammonia + N-Pentylpiperidine $\xrightarrow{K_7}$ $\overline{|Piperidine|}$ + Pentane
+H_2

K_4

+H_2 K_3 \+PIP

Pyridine $\underset{+3H_2}{\overset{K_1}{\rightleftarrows}}$ $|Piperidine|$ $\xrightarrow[+H_2]{K_2}$ Pentylamine $\xrightarrow[+H_2]{K_6}$ Ammonia + Pentane

+MPA

K_5

Ammonia + Dipentylamine $\xrightarrow[+H_2]{K_8}$ Pentylamine + Pentane
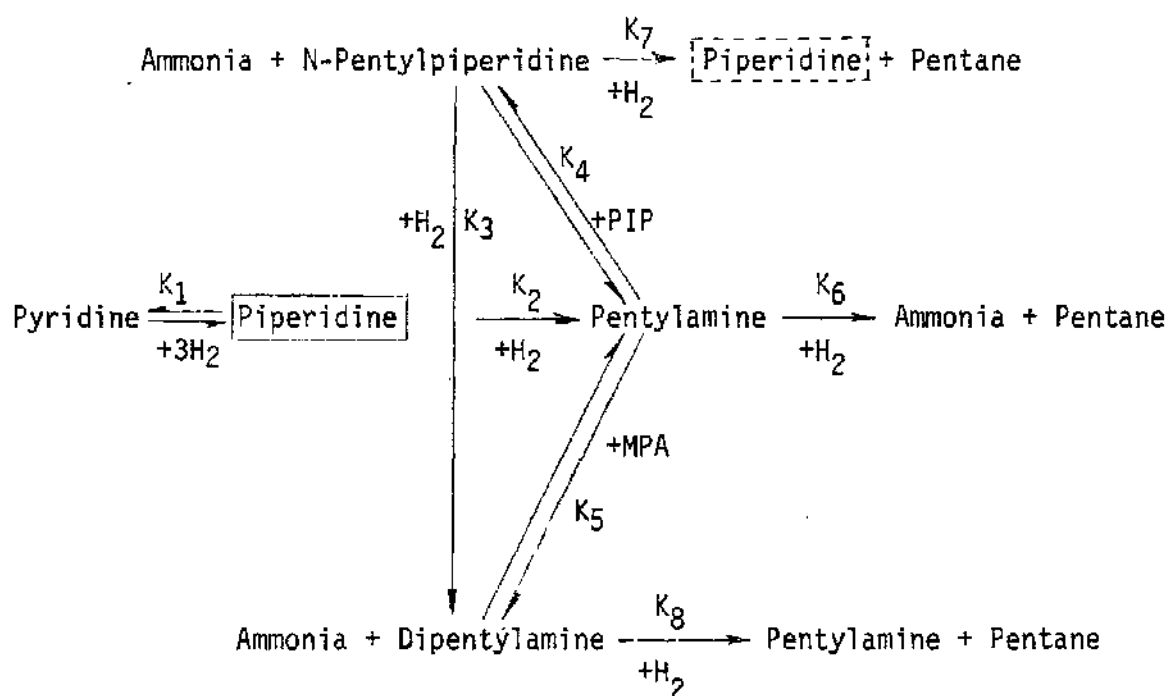
Piperidine (PIP) hydrogenolysis proceeds via ring opening to pentylamine (MPA), followed by alkyl transfer from pentylamine to piperidine (N-pentylpiperidine and ammonia are formed). Hydrocracking of these bases (which is rate determining) leads to the formation of pentane and NH_3. Although the RDS involves C-N hydrogenolysis, it is also influenced

by the equilibrium constants for the alkyl transfer reactions.

The conversion of pyridine at high pressures of hydrogen is similar in both activity and selectivity for $CoO-MoO_3/Al_2O_3$ and MoO_3/Al_2O_3 catalysts (73). This may indicate that CoO merely adds hydrogenation activity and that C-N hydrogenolysis which is rate determining, occurs predominantly on Mo sites. If this is correct, high Co/Mo ratios are expected to give a lower HDN activity. The following surface mechanism was suggested for surface C-N hydrogenolysis:
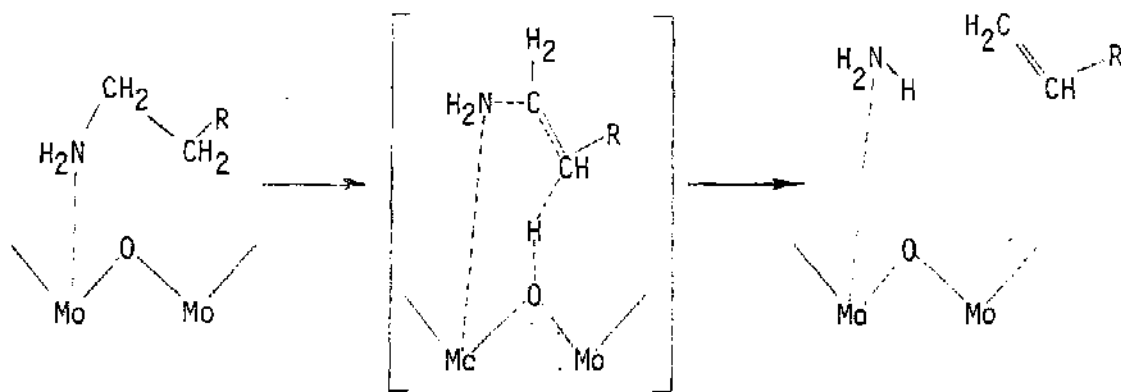
The NH_3 desorbs and the olefin is quickly hydrogenated. This sequence is supported by the fact that trace amounts of pentenes have been observed during pentylamine hydrogenolysis (76). This mechanism suggests that increasing the Mo-N surface interaction should increase the rate of HDN. This aspect will be discussed later.

3. MULTI-RING HETEROCYCLES

In the past, kinetic studies with multi-ring heterocyclic nitrogen compounds have been difficult to perform because of side reactions, instability of intermediates which lead to coking, and the analytical difficulties in identifying products. Working at differential reactor conditions and the use of modern analytical procedures should reduce these problems considerably. Unfortunately,

there have been very few studies over the last ten years in this area
(75, 82, 83). Most of the available data are from older work (80, 81, 84).

One extensive investigation was that conducted by Doelman
and Vlugter (81), who studied the hydrodenitrogenation of quinoline
on unsulfided cobalt molybdate catalysts at 300-850°F and 600-1800 psig.
The unsulfided condition is emphasized here because as discussed later,
sulfiding can significantly affect the course of the HDN mechanism.
These workers identified tetrahydroquinolines, anilines, and aliphatic
amines in the products, and concluded that these are intermediates.
A reaction sequence was postulated in which quinoline is hydrogenated
to 1,2,3,4-tetrahydroquinoline (THQ), which subsequently hydrocracks
to either o-propylaniline or 3-phenyl-propylamine. The final step
was postulated to be HDN of the aniline or amine to NH_3 and hydro-
carbon. By comparing HDN rates for quinoline with those for aniline
and amines, these workers concluded that the rate-determining step for
HDN of quinoline is hydrogenolysis of the C-N bond in an aniline
structure.

Tsusima and Sudzuki (87) observed decahydroquinoline (DHQ)
as well as the tetrahydroquinolines (THQ) over nickel-type catalysts.
Their work and that described above by Doelman and Vlugter (81)
suggests that the following equilibrium may occur during HDN of
quinoline (Q).
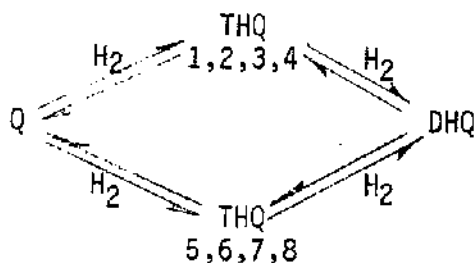
The 1,2,3,4-THQ is then hydrocracked to give alkyl-anilines which subsequently undergo HDN, the rate-determining step. DHQ hydrocracks to primary and secondary amines which can then denitrogenate to either alkyl benzenes or alkyl cyclohexanes, depending on the hydrogen pressure.

The effects of methyl substitution on the quinoline ring may also be noted. In general, it is found that methyl substitution on a ring makes hydrogenation of that ring more difficult (88). However, very little experimental work has been done to study the kinetic effects of such substitution. More information of this type exists for HDS than for HDN, and will be mentioned in the next section.

A recent study of HDN of multi-ring heterocycles over un-sulfided cobalt molybdate catalysts suggests that quinoline rings and indole rings show different rate-determining steps (75). These authors suggest the following:
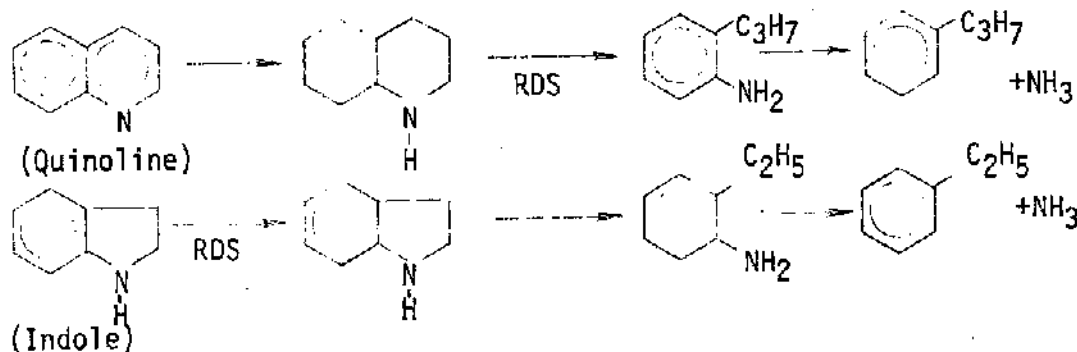
In the case of indole, hydrogenation of the five-membered ring appears to be the rate-determining step, whereas for quinoline hydrocracking of the half-saturated quinoline ring is reported as the slow step for HDN. However, this system was by no means a detailed kinetic study, and was conducted at high conversion levels in an autoclave. Therefore, product inhibition and other complications cannot be dismissed.

· Clearly, there are indications of plausible mechanisms, as well as reasonable reaction schemes for hydrodenitrogenation of multi-ring heterocycles. However, a detailed understanding of the kinetics of pertinent steps is lacking.

4. INTERACTION OF HDN AND HDS REACTIONS

There has been some work carried out over the past few years which indicates the simultaneous interactions between HDS and HDN reactions (78, 79). The motivation for this work stems from observations of unusual synergistic effects during HDN using an HDS process and vice versa.

For example, Goudriaan (89) and co-workers studied the HDN of pyridine over a cobalt molybdate catalyst at temperatures of 250-400°C and a pressure of 1200 psig. They found that at high conversion levels, the temperature required to attain a certain degree of nitrogen removal is about 25°C lower with a sulfided catalyst than with the catalyst in its oxide form. The presence of H_2S results in a further reduction of this temperature requirement by 60°C. They subsequently found that hydrogenation of pyridine to piperidine is 25-45 percent higher on the presulfided catalyst than on the oxide catalyst. The presence of H_2S has little effect on this step. However, ring opening of piperidine to pentylamine was faster on the sulfided catalyst than on the oxide catalyst, and also increased significantly with the addition of H_2S. They concluded that the beneficial effect of H_2S on HDN of pyridine is twofold. First, the hydrogenation activity of the sulfided catalyst is substantially greater than the oxide catalyst for the conversion of pyridine to piperidine. Second, the presence of H_2S has a beneficial effect on the hydrocracking

activity of the catalyst.

Similar effects were reported by Mayer (78) who found that nitrogen compounds severely inhibit HDS of thiophene with sulfided cobalt molybdate catalysts, but that H_2S promotes HDN activity. The explanation given for the latter is that H_2S increases the hydro-cracking activity of the catalyst, and therefore the rate of cracking of piperidine to n-pentylamine which is assumed to be the rate-determining step.

5. IMPLICATIONS FOR FURTHER RESEARCH

Hydrodenitrogenation is an important area which has not re-ceived the detailed study necessary to understand the nature of nitrogen removal from multi-ring compounds. However, two key findings result from the work to date. First, hydrogenolysis of C-N bonds is a central step for many HDN reactions and indeed may generally be rate-determining. Second, the degree of presulfiding and the presence of H_2S can have significant promotional effects on HDN reactions. Each of these effects should be exploited to obtain more active and selective HDN catalysts.

To synthesize new catalytic materials with higher activity for C-N hydrogenolysis, it is likely that bifunctional systems can play a significant role. For example, a controlled acid function may interact just sufficiently with the basic nitrogen atom, while an adjacent surface site (perhaps a transition metal cation) interacts with the ∝-carbon atom in the nitrogen heterocycle. This could lead to substantial weakening of the C-N bond in the heterocycle and perhaps an increase in activity. Metal-support interactions and novel sulfides, oxides, and oxysulfides (see Part 2) are likely to be

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important for this aspect of HDN research.

The implications of the above concepts as well as other aspects of HDN chemistry will be discussed in further detail in Part 3 for specific processes.

E. HYDRODESULFURIZATION

1. GENERAL REMARKS

As mentioned in the previous section, hydrodesulfurization (HDS) has been studied to a greater extent than hydrodenitrogenation (HDN) because of the relatively higher levels of sulfur compared to nitrogen in petroleum crudes. Substantial amounts of sulfur are also found in coal, and a recent study (90) shows that the structures of the sulfur-bearing molecules in coal liquids are quite similar to those present in petroleum crudes. These include thiophenes, benzothiophenes, and naphthobenzothiophenes (90). However, even from the work which has been done to date in this area, it is still difficult to ascertain key mechanistic steps for the HDS of representative model compounds. A detailed mechanism would be of value in providing a basis for the development of new and improved catalysts.

The following discussion is divided into three parts, overall kinetic effects and mechanistic considerations for single ring and multi-ring sturctures. The implications of this work for research are discussed in the last section. This serves as an introduction to the analysis of Part 3.

2. GENERAL KINETIC EFFECTS

The literature concerning HDS chemistry and catalysis has been

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reviewed in some detail elsewhere (91-93). Significant contributions
in the area of kinetics have been made by Kemball and co-workers
(94-97) who studied the reaction of sulfur compounds over MoS_2 and
WS_2, and by Amberg, et al. (98-103) who used Cr_2O_3, MoS_2, and cobalt
molybdate as catalysts for the HDS of thiophene and related compounds.
Most of this work was with single ring compounds such as thiophene
and tetrahydrothiophene, or with alkyl thiols. The most significant
work with multi-ring sulfur compounts was done by Givens and Venuto
(104) and will be discussed later. Although HDS catalysis is complex,
some generalizations can be made.

    a.   Effects of the Sulfur Compound

At high partial pressures of hydrogen, the rate of HDS
is approximately first order with respect to the sulfur compound. The
rate and order both decrease with increasing concentration of sulfur
compound (and thus decreasing partial pressure of H_2) and at high
concentrations the rate can become inversely proportional to the con-
centration. For example, this behavior has been observed for thiophene
desulfurization over Ni_3S_2 (105, 106) or MoS_2 (105, 107). This suggests
that the surface coverage of sulfur compound increases with pressure
and that at high pressures this effect decreases the rate of reaction.

The fact that the hydrogenolysis of thiophene over MoS_2
and Ni_3S_2 is slower than that for tetrahydrothiophene over the same
catalysts indicates a possible two-point adsorption for thiophene and
a single-point adsorption for its saturated analog (105). This in-
formation is useful in considering various catalytic means for activating
sulfur-containing molecules.

As will be shown later, the rate of desulfurization

usually decreases with increasing molecular weight of the sulfur-containing molecule. In some cases this can be attributed to steric effects (104, 108), in others to electronic factors (104), however, the situation is far from clear because of complicating factors, such as catalyst deactivation, which occur for higher molecular weight species.

b. Effects of Hydrogen

In general, the rate of desulfurization increases with increasing partial pressure of hydrogen (91, 98-103).

c. Effects of Additives

The effects of various additives on the rate of HDS depends on the nature of the catalyst. However, some general remarks can be noted. The effect of H_2S at the 2-3 mole percent level is usually minimal, but at higher concentrations there are reports that it inhibits HDS activity (100, 101). For example, it slightly decreases the rate of HDS of thiophene over MoS_2, Cr_2O_3, and cobalt molybdate catalysts (100). As mentioned above, this behavior is similar to that observed for an increase in partial pressure of the sulfur-containing reactant to be desulfurized. H_2S also inhibits butene hydrogenation (but not for butadiene) (98, 101). This effect is greater than the overall decrease in rate for thiophene HDS suggesting that H_2S competes for butene hydrogenation sites (98, 101) (see mechanistic discussions below).

The addition of <u>oxygen</u> to thiophene during HDS over MoS_2 causes a doubling of the rate followed by a decrease over a period of hours to the original value without any change in product composition (100). The effect of oxygen on butene (a proposed intermediate in thiophene HDS) hydrogenation is even greater, increasing by

one hundredfold. This effect is unexplained. However, it has been speculated that it may be due to the formation of a more active oxy-sulfide surface (109).

Hydrogenolysis of thiophene over MoS_2 by various compounds decreases in the order cyclopentadiene $> CS_2 > C_2H_4 > H_2S > SO_2 > CH_4 > CO$ (105). All of these molecules affect the rate of reaction reversibly except cyclopentadiene which has similar molecular dimensions to those of thiophene. It has been suggested that the former adsorbs by a two-point mechanism on the same sites which activate thiophene and reduces its surface concentration.

d. Bond Activation

Kinetic studies of HDS reactions over MoS_2 and WS_2 by Kemball, et al. (95) show that the relative ease of scission of various chemical bonds is H-H $>$ H-S $>$ C-S $>$ C-H (C_2H_6) $>$ C-H (CH_4) $>>$ C-C. The cleaving of C-S bonds in straight chain compounds is easier than in cyclic compounds (97).

3. HDS OF SINGLE RING COMPOUNDS

Most of the mechanistic and kinetic work in the area of HDS has been done with thiophene because this molecule has been considered to be the simplest model for sulfur-containing molecules in both petroleum and coal (90, 92). The more recent work has been done by Kemball (94-97) and Amberg (98-103).

Kemball's studies give useful information concerning relative bond strengths (see above) and the nature of transient intermediates. His work indicates that the rate-determining step for desulfurization to saturated hydrocarbons is the combination of an adsorbed alkyl radical with a chemisorbed hydrogen atom to form the alkane which rapidly

desorbs (97). This is in reasonable agreement with Amberg's work.

Among the most significant kinetic studies done in flow systems are those by Amberg and co-workers (98-103). Reaction schemes for thiophene desulfurization over chromia and cobalt molybdate catalysts and the relative rates for the various steps are shown in Figure VII-1. For both catalysts, reaction of adsorbed olefin with hydrogen to form butane appears to be rate limiting. This work also suggests that the first reaction of thiophene in the primary reaction path is the C-S bond cleavage to form 1,3-butadiene, rather than hydrogenation of the C=C bonds in thiophene. These workers also found that H_2S inhibits the desulfurization of thiophene and the hydrogenation of butene, but that it had very little effect on cis-tran isomerization, butadiene conversion to butenes, or double-bond isomerization. This suggests that more than one kind of site is involved in HDS. The identification of these sites would be useful for the development of more active and selective HDS catalysts.

4. MULTI-RING HETEROCYCLES

Very few kinetic studies have been done with multi-ring sulfur heterocycles. The work by Givens and Ventuo is perhaps the most significant (104). These workers studied the HDS of various substituted benzothiophenes in a flow system at 400°C and atmospheric pressure over cobalt molybdate catalysts. They showed that certain common reaction paths are apparently involved. This can be illustrated for the reaction of 3,7-dimethylbenzo b thiophene which indicates that the following general reactions take place:

    A. Alkyl group migration on the thiophene ring

    B. Dealkylation from the thiophene ring
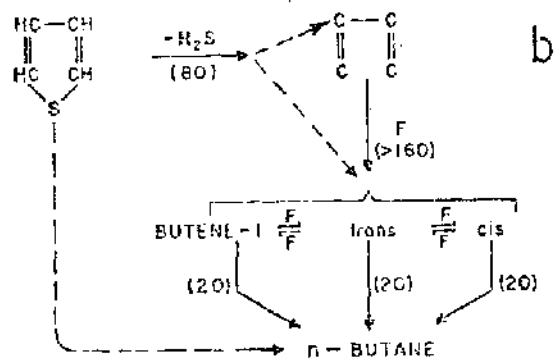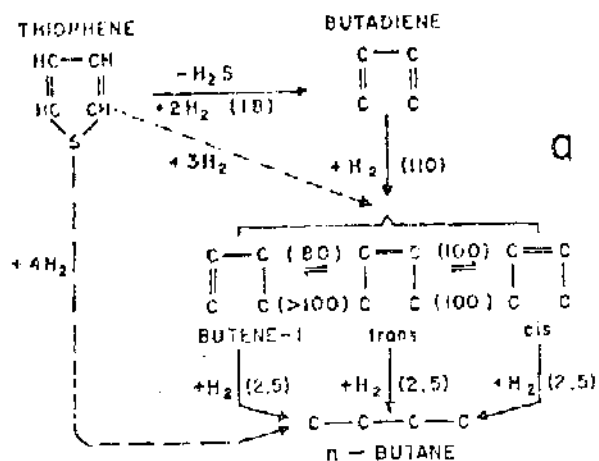
REACTION SCHEMES AND ESTIMATES OF RATES AND STEPS
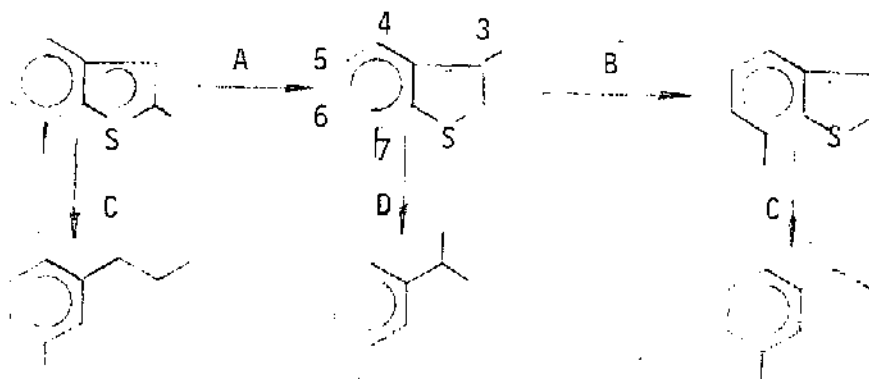
Micromoles Per Gram of Catalyst Per Second

    a.   Chromia at $415^{\circ}C$

    b.   Cobalt Molybdate at $400^{\circ}C$

FIGURE VII-1 (101)

C. Sulfur extraction from rearranged or demethylated secondary products

D. Direct sulfur extraction from the primary reactant

These reactions are shown in the following sequence:

It was also found from reactions A-C that the benzene ring is relatively inert with respect to dealkylation or methyl migration. However, conversions, product distribution, and selectivity to various products were found to be highly dependent upon the number and position of the alkyl groups. Conversion, for example, decreased with increasing alkyl substitution. Alkyl groups on the thiophene ring were found to lower conversion and HDS selectivities more than alkyl groups on the benzene ring. Also, benzothiophenes were found to be significantly less reactive with respect to HDS than thiophene.

Detection of dihydrobenzo b thiophenes at high space velocities suggested that these compounds are intermediates in the above HDS reactions. Furthermore, it was found that the desulfurization step involves C-S bond breaking as an initial step, and that aromatic saturation is not a prerequisite for C-S bond breaking when the S-atom is

attached to an aromatic C. No evidence was found for significant amounts of C-C bond scission.

It should be noted that these conclusions concerning the mechanism of HDS are qualitative, and not the result of a detailed kinetic study. Also, there are no indications that the same product distribution would be observed at higher pressures. However, the study of Givens and Venuto gives an indication of the type of chemistry which is important for removing sulfur, as well as relative rates for various reactions of interest. Similar studies have been reported recently by Phillipson (110) and Frye and Mosby (111), however, much work still needs to be done with these multicyclic systems.

5. IMPLICATIONS FOR FURTHER RESEARCH

The work to date in the HDS area indicates that hydrogenolysis and hydrogenation reactions proceed on separate catalytic sites. Selective poisoning experiments by Amberg and co-workers suggest that hydrogenation reactions occur on strongly electrophilic sites, whereas desulfurization reactions proceed on weakly electrophilic sites (103). This should be further explored and verified. If true, it suggests that more active catalysts will require a bifunctional approach, and many of the concepts discussed in previous sections will be applicable. Catalyst-support interactions, controlled surface acidity, and crystal-lite-size effects are just a few which could be important.

The nature of surface sulfidation and its relationship to HDS catalysis is another important area that should be further explored. Novel catalyst preparative procedures and new materials could play a key role in this area. The former should be especially important for the synthesis of novel catalytic materials in high surface area.