As an example, materials of the general stoichiometry $M_2Mo_3O_8$ (where M = Mg, Zn, Co, Mn, and others) have been suggested for study as HDS catalysts (109) because of the unusual position of the Mo atoms in these structures. They are located at the apices of equilateral triangles with a Mo-Mo distance 2.53 Å (shorter than in Mo metal). However, only recently has a procedure been developed to prepare these materials in high surface area (112). They were indeed found to exhibit unusual catalytic properties for hydrogenation and hydrogenolysis reactions, with activities somewhat between those observed for metals and oxides (112). The application of new catalytic materials will be discussed more extensively in Parts 2 and 3 of this study.

Finally, mechanistic studies can be useful in discerning the role of intermediates such as olefins and diolefins in coke formation. This has important consequences in catalyst deactivation and the regeneration problems discussed earlier in this report.

F. POLYNUCLEAR AROMATIC CRACKING

Most of the accepted models concerning the structure of coal treat it as a highly condensed polynuclear aromatic substance. The broad objective in coal liquefaction is to selectively crack this structure with a minimum consumption of hydrogen. In general, this gives high yields of low molecular weight aromatics and low yields of light gases. The function of hydrogen is to "heal" those carbon atoms involved in C-C bond scission, and also to form H_2S and NH_3 for heteroatom removal. Clearly, whether the product objective is boiler fuel or high octane gasoline, catalyst selectivity is important for controlling hydrogen utilization and the final product distribution. Therefore, studies of the effects of catalytic properties on the selectivity patterns for polynuclear hydrocracking reactions are useful in this respect. Unfortunately, only minimal work has been done in this area, primarily because of the experimental difficulties in carrying out a catalytic study with large aromatic molecules. These difficulties include rapid catalyst deactivation and, more particularly, difficulties in obtaining reliable product analyses. However, over the past five years, chromatographic and mass spectrographic techniques have been developed which are capable of giving more accurate analyses (1, 2). A number of studies in this area have appeared in this period. This section gives a brief summary of these studies. After some general comments, the discussion is divided into mechanistic considerations for the hydrocracking of four representative model structures, naphthalene, anthracene, phenanthrene, and pyrene. Some general comments are given concerning catalyst differences and deactivation. The last section gives a discussion of implications for further research in areas relevant for the catalytic conversion of coal.

1. GENERAL COMMENTS

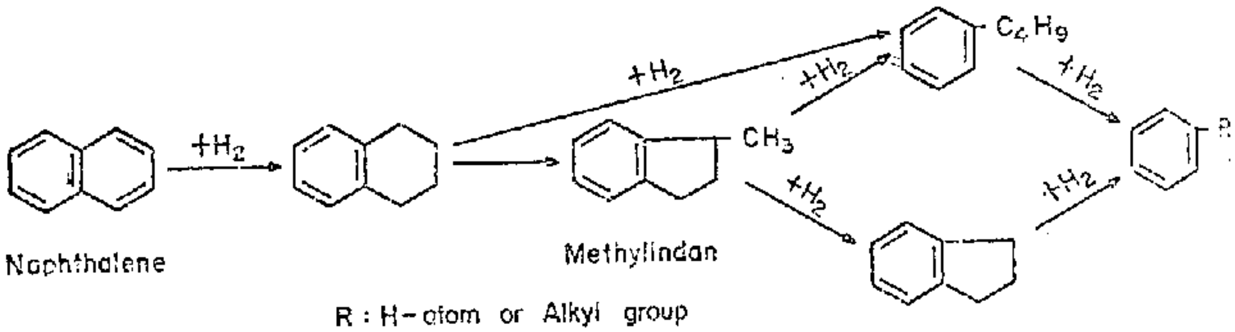
The hydrocracking of polynuclear aromatic hydrocarbons has been reported to proceed through a multi-step mechanism involving hydrogenation, isomerization, cracking, and rehydrogenation, in that order (114, 115). This follows from a number of studies such as those by Cawley (116) who studied hydrocracking of naphthalene over MoO_3, and obtained alkylbenzenes and benzene as the main products. Similarly, the primary reactions observed during the hydrocracking of tetralin, anthracene, phenanthrene, and pyrene over nickel sulphide on silica-alumina were found to be hydrogenation, isomerization, alkylation, cracking, and paring (117-119). The latter reaction is an unusual one which is frequently observed for the hydrocracking of naphthenes (120). In effect, a reaction occurs which pares methyl groups from cycloparaffin rings (naphthenes) and eliminates them as branched paraffins, mainly isobutane, in such a way that rings are conserved. Finally, in recent studies anthracene conversion to benzene was found to take place in a stepwise manner through the formation of hydroanthracenes and naphthalenes (121). These effects are described more fully in the following discussion concerning the hydrocracking of specific compounds. Much of the work described in this section was done by Qader and co-workers (114, 115, 122) who carried out their studies using an autoclave at 475°C and pressures of 1000-2000 psig. The catalysts used were CoS, MoS_2, NiS, and WS_2, which were physically mixed with silica-alumina to give a cracking component.

2. NAPHTHALENE

Studies of naphthalene hydrocracking (114, 115) suggest that naphthalene is first hydrogenated to tetralin. Tetralin is then isomerized to methylindan which subsequently dealkylates to indan. Benzenes appear to form from indan and/or tetralin by C-C bond scission. These data are consistent with a sequence of hydrogenation, isomerization, and cracking reactions as shown in Figure VII-2. At very high conversions butylbenzenes form in significant amounts, probably through direct ring opening reactions for tetralin and/or methylindan.

3. ANTHRACENE

In their hydrocracking studies of anthracene, Qader and co-workers (114, 115) found that this molecule is first hydrogenated to hydroanthracenes in a stepwise fashion forming di-, tetra-, and



MECHANISM OF NAPHTHALENE HYDROCRACKING

FIGURE VII-2 (114)

octahydroanthracenes, respectively (see Figure VII-3). These workers suggest that the saturated six-membered rings of tetra- and octahydroanthracenes are then isomerized to five-membered rings (hydroanthracene isomers) which subsequently crack to naphthalene. The naphthalenes are converted to benzenes through tetralins and indans as described above. It should be noted from the scheme given in Figure VII-3 that preferably one would like to selectively crack the center ring in the dihydroanthracene intermediate (to alkyl benzenes) before it consumes additional hydrogen by further hydrogenation and dealkylation reactions.

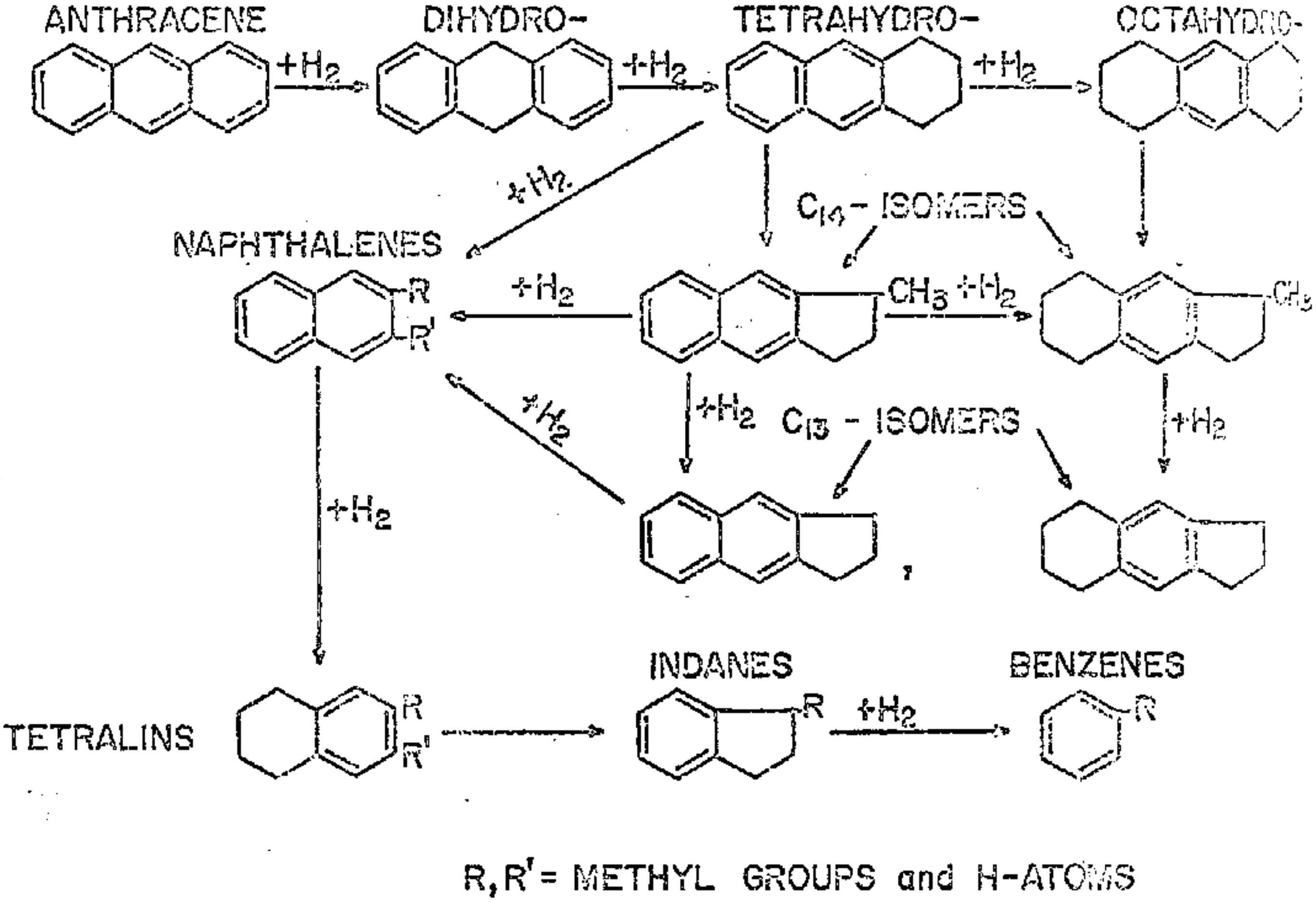
4. PHENANTHRENE

Phenanthrene hydrocracking has been studied in some detail by Sullivan and co-workers (118-120) over several hydrocracking catalysts. The principal products are tetralin and methylcyclohexane. These workers indicate three types of reactions.

a. Saturation and cleavage of one of the terminal rings to form a paraffin and a bicyclic such as tetralin. This reaction is generally insignificant as paraffin yields are usually small.

b. Ring saturation and cleavage of the central ring. This accounts for most of the methylcyclohexane and ethylcyclohexane formed. For minimum hydrogen consumption one would prefer to saturate and crack only the center ring to form ethyl- and methyl-benzenes. This has not been observed.

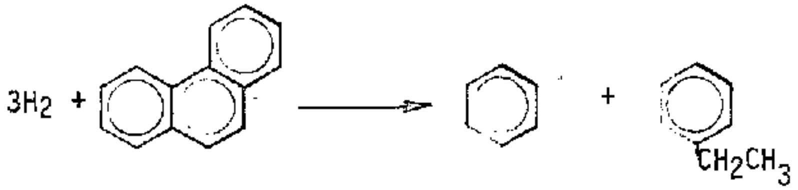
c. An unusual cracking reaction which produces bicyclic hydrocarbons, principally tetralin, without giving equivalent amounts of light paraffins. This is the predominant reaction, a mechanism for which is suggested elsewhere (120).



MECHANISM OF ANTHRACENE HYDROCRACKING

FIGURE VII-3 (114)

Some center-ring cracking of phenanthrene is indicated by the work of Wu and Haynes (123). Their approach was to control the selectivity of this reaction by using a Cr_2O_3-Al_2O_3 catalyst with low acidic strength. They point out that Cr_2O_3-Al_2O_3 catalysts also tend to be more resistant to poisons and that the alumina matrix stabilizes the chromium ion to prevent reduction below Cr^{+3} in a reducing environment. The presence of biphenyl and 2-ethylbiphenyl in significant quantities indicated that a certain fraction of the reaction involved center-ring cracking, the desired reaction:



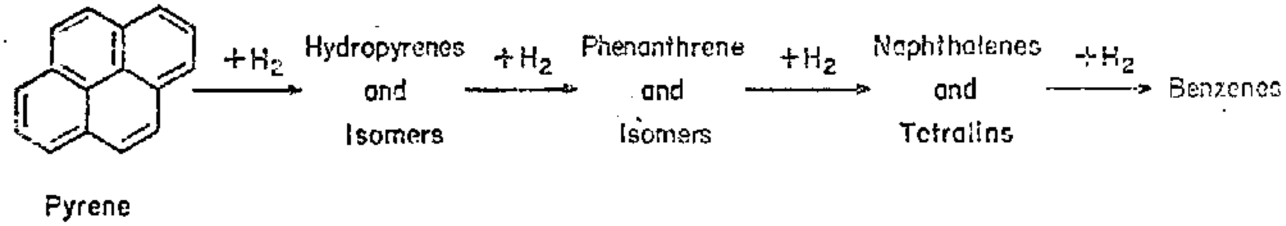
Therefore, controlled acidity in the presence of transitional metal cations such as chromium may be an approach to enhancing the selectivity of center-ring cracking reactions.

5. PYRENE

Highly condensed polynuclear aromatics tend to be refractory and difficult to study for catalytic reactions. Such is the case for pyrene. The hydrocracking mechanism is highly complex. The pattern shown in Figure VII-4 is suggested by Qader (114). As with the case for naphthalene and anthracene, it indicates that the reactions occur stepwise through hydrogenation, isomerization, and cracking.

6. EFFECTS OF CATALYST COMPOSITION

For convenience, most of the above mentioned studies have been



MECHANISM OF PYRENE HYDROCRACKING

FIGURE VII-4 (114)

carried out in autoclaves. This procedure has many advantages. However, at high conversion levels specific catalytic activities are disguised by catalyst deactivation effects and product inhibition. Physical characterization of the catalyst before and after reaction would be useful in isolating and identifying these problems. Unfortunately, while the studies by Qader and co-workers (114, 115, 122, 124) are among the more significant ones for the present discussion, the catalyst was only characterized in very few cases. Even simple BET surface areas are seldom given. Therefore, it is difficult to evaluate relative differences between the various catalysts studied. However, in general, these authors find that CoS mechanically mixed with silica alumina appeared to be the most active hydrocracking catalyst among the simple sulfides tested (MoS_2, NiS, and WS_2). This is probably due to the facile formation of saturated rings which then readily isomerize or crack. It was also found that catalysts with lower levels of alumina were more active for hydrocracking than those with higher alumina content. However, the CoS catalysts gave lower yields of coke on the catalyst. This may be due to the relatively higher hydrogenation activity of these catalysts which may prevent deposition of unsaturated coke precursors on the catalyst surface. The coke yield increased with the molecular weight of the polynuclear aromatic tested.

7. PERSPECTIVE FOR FURTHER RESEARCH

Recent studies concerning the hydrocracking of polynuclear aromatics give a perspective for the types of reactions which can occur during coal liquefaction and coal liquids refining. There is a need to carry out some of these same studies at differential reactor conditions where product inhibition, catalyst deactivation, and heat and mass transfer effects are minimized. This should be done in conjunction with the correlation of mechanism changes with known properties of well characterized catalysts. The ultimate objectives of this work should be to maximize the yield of lower molecular weight aromatics, and to minimize hydrogen consumption and the yield of light gases. In most instances this requires ring cleavage along the center of symmetry. Although some progress has been made in this direction (123), there is much work to be done.

Controlled activity and selectivity will certainly require multi-functional catalysis. A controlled hydrogenation and cracking activity may be central to the solution of this problem. Materials such as many of the complex oxides, sulfides, and oxysulfides discussed in Part 2 of this study may well provide a controlled hydrogenation activity which is stable at the conditions of liquefaction or upgrading. Furthermore, numerous new solid acids can now be prepared and characterized (125). These materials, in combination with the proper hydrogenation function, could give catalysts with increased activity and activity maintenance, while still retaining the desired product distributions. Application of these concepts to the specific needs of several coal conversion processes will be discussed in Part 3.

G. CARBON/COAL GASIFICATION

1. GENERAL DESCRIPTION OF GASIFICATION CHEMISTRY

The primary objective in coal gasification is to produce high BTU gas ($>$ 900 BTU/SCF). Those aspects of the gasification process which are directly concerned with chemical conversions and amenable to improvement by catalysis can be divided into four areas.

i. Devolatilization in the gasifier, producing CH_4, CO, CO_2, tars, and liquids;

ii. Gasification of residual char at 1800°F with H_2 or H_2O/O_2 mixtures to form CH_4, CO, and H_2;

iii. Water-Gas Shift catalysis of the $CH_4/CO/H_2$ mixture to a H_2/CO ratio of approximately 3;

iv. Methanation catalysis of the residual CO/H_2 mixture to CH_4;

Methanation and water-gas shift catalysis have already been discussed in Sections VII-B and VII-C, respectively. Therefore, the present section will treat only devolatilization, and, in greater detail, gasification.

2. DEVOLATILIZATION

Devolatilization of coal is an important reaction because it forms CH_4 in the gasifier. From the thermal efficiency point of view, this is the most effective means to produce CH_4, in particular when compared to the gasification-methanation route. Two major reactions give rise to CH_4 formation during coal devolatilization:

$$C_nH_m \longrightarrow \left[(4n-m)/4\right] C + (m/4)\, CH_4 \qquad \text{(Hydrocracking)}$$

$$C_nH_m + \left[(4n-m)/2\right] H_2 \longrightarrow nCH_4 \qquad \text{(Hydrogenolysis)}$$

The first reaction can be considered to be H_2 transfer within the coal "molecule". The second is essentially the reaction of H_2 with C-C bonds to form CH_4.

Very little definitive catalytic work has been done on devolatilization, although it is well known that the presence of Lewis acids such as $ZnCl_2$ or $SnCl_2$ tends to increase the yield of gaseous products (including CH_4) and decrease the amount of coke formed (126). Similarly, it was discovered some years ago that the gas yield could be substantially affected by the temperature-time history of the coal (127). For example, if coal is heated very rapidly (thousands of degrees per second) the yield of liquid and gaseous products can be increased significantly. In a simplistic way, this phenomenon can be considered as consisting of two parallel and competing reactions. One is a decomposition of the coal "molecule" to $CH_4/CO/H_2$, light gases, and liquids, the other a graphitization or polymerization reaction. The latter process is likely to have a much lower activation energy than the fragmentation reaction because it probably involves chain steps and radical recombination. Therefore, rapid heating to high temperatures should favor the first reaction to light gases. A number of studies have been done in this area with some reports that as much as 60 percent of the organic matter in coal can be volatilized in this manner. The Garrett pyrolysis process is based on this concept.

Although much of the chemistry in this area is thermal and involves free-radical type reactions, there may be opportunities for the use of catalysis to increase CH_4 and liquid yields, and possibly to control the product distribution. Very little work has been done in this area. The major problem involved in using catalysis in this area is a common one for catalytic gasification in that it is necessary to contact a solid reactant (coal) with a catalyst which is also a solid or, probably at best, a liquid. While gaseous catalysts are not excluded, it is unlikely that they would be as effective as a solid or liquid catalyst.

3. GASIFICATION

Studies of coal or carbon gasification have primarily been concerned with the following reactions:

$$C + 2H_2 \rightleftharpoons CH_4 \qquad (A)$$

$$2C + 3/2\ O_2 \rightleftharpoons CO_2 + CO \qquad (B)$$

$$C + CO_2 \rightleftharpoons 2CO \qquad (C)$$

$$C + H_2O \rightleftharpoons CO + H_2 \qquad (D)$$

The most desirable of these, for technological reasons, is reaction (D), i.e. steam gasification. However, as discussed below, there are important thermodynamic and kinetic constraints involved with this reaction. The other reaction of primary interest is (A), i.e. hydrogasification. All of the reactions mentioned (A-D) have been studied in detail by a number of investigators both with and without the addition of catalytic components. Much of this work is described by numerous authors in the series by Walker (128). However, it should be noted that much of the mechanism work is speculative, primarily because of the complexity of the systems involved, but also because many of these studies do not include sufficient characterization data for the carbon-catalyst system. Admittedly, the problem is a difficult one because the systems studied frequently involve a solid catalyst. Dynamic changes at the coal- or carbon-catalyst interface make characterization difficult. Therefore, rate-controlling steps are often speculated to vary substantially with the extent of reaction. Heat and mass transport limitations are also often encountered. Some studies which are representative of this area are given in this section.

Extensive work has been done for CO_2 and O_2 gasification of carbon (128). However, the present discussion is limited to steam gasification and hydrogasification.

a. Steam Gasification

For the steam gasification of coal the key reaction is that of steam plus carbon to form CO and H_2 (reaction D above). This reaction is very endothermic (+31.4 kcal/mole). In most existing processes the heat for this reaction is supplied by the direct combustion of coal with air or O_2. The supply of thermal energy in this part of the process can account for as much as 1/3 of the process cost. The chemical dilemma in steam gasification can be considered as an inefficient thermal balance. This is apparent from the following reactions.

	$\Delta H_{298^\circ K}$ (kcal/mole)	Reaction Temperature
Gasification		
$2C + 2H_2O \longrightarrow 2CO + 2H_2$	+ 62.76	1000°C (1800°F)
Shift		
$CO + H_2O \longrightarrow CO_2 + H_2$	- 9.83	300°C (600°F)
Methanation		
$3H_2 + CO \longrightarrow CH_4 + H_2O$	- 49.27	400°C (700°F)
$2C + 2H_2O \longrightarrow CH_4 + CO_2$	+ 3.66	

Thus, the sum of the reactions which give rise to the formation of CH_4 are nearly thermoneutral. However, in existing technology water-gas shift and methanation steps are carried out at much lower temperatures for reasons of thermodynamics and catalyst maintenance. Therefore, the exothermic heat generated in these two steps cannot be efficiently utilized at the higher temperature for gasification. The solution to the problem is catalytic gasification of coal at 800-900°F. Then the heat from the shift and methanation steps can be used for the gasification reactions. This possibility of a "single step" gasification has been a primary motivating force for catalytic steam gasification.

For the steam gasification reaction alkali metal oxides and carbonates have been found to be among the best catalysts. During reaction, it is likely that the salt is molten and probably oxygen deficient. The molten state may lead to increased mobility and thereby enhance coal-catalyst contact for more effective gasification. A recent study by Willson and co-workers (129) found that K_2CO_3 was an active catalyst for the steam reaction at 650°C and 2 atm pressure, especially at levels of about 20 weight percent. Similar results are reported by Haynes, et al. (130) who found that alkali metal compounds are among the most effective carbon gasification catalysts when steam is used as an oxidant. Gasification rates were increased by 30-66 percent by using 5 weight percent alkali metal.

To have a "single-step" gasification reactor, the gasification, water-gas shift and methanation reactions must be catalyzed simultaneously. This requires a bifunctional catalyst. Catalysis of the steam reaction has already been mentioned. The water-gas shift and methanation reactions are usually catalyzed by metal catalysts such as Ni or Fe. Consequently, combinations of Ni and other transition metals with the alkali metal oxides or carbonates have been explored as "single-step" gasification catalysts (129-131). The results are encouraging. However, massive amounts of catalyst are usually required for effective activity. A recent patent in this area (131) describes a related process which takes advantage of the catalytic properties of alkali metal catalysts for gasification. However, instead of having a methanation constituent, increased hydrogen partial pressures are used in the gasifier. This gives rise to a substantial increase in hydrogasification (see below), and in principle methane is produced by a thermoneutral process.

b. Hydrogasification

As mentioned previously, the direct combination of H_2 with coal to form CH_4 occurs to a limited degree in many gasifiers, and is highly desirable because it is exothermic (-17.9 kcal/mole carbon), and therefore reduces heat requirements to drive the endothermic carbon-steam reaction. Unfortunately, this reaction is kinetically very slow. Furthermore, it is thermodynamically favored by high pressures and low temperatures, and therefore a catalyst is needed. The relative gasification rates of carbon with H_2 and other gases are illustrated by data of Walker and co-workers (132), obtained at 800°C and 1 atm pressure with no catalyst present.

	Relative Rate
$C-O_2$	10^5
$C-H_2O$	3
$C-CO_2$	1
$C-H_2$	10^{-3}

Clearly, the hydrogasification reaction is very slow compared to other gasification reactions. However, several recent catalytic studies (132-136) have been reported for the C-H_2 reaction, and indicate some promise.

For example, Rewick and co-workers (134) studied the change in reactivity of carbon with H_2 in the presence of various catalysts. With Pt over an extensive temperature range, these workers found that the rate of CH_4 formation was approximately equal to the rate of H_2 dissociation to atomic hydrogen. Therefore, the catalytic effect is interpreted as an enhancement of H_2 dissociation on the metal surface, followed by surface diffusion across the metal/carbon interface and reaction with carbon to form CH_4. Interestingly, the reaction rate of carbon with H_2O was also increased by more than an order of magnitude by the presence of small amounts of Pt metal on the surface of the carbon. However, in this case CO and H_2 were primary products. For the hydrogasification reaction to CH_4 it would appear that the rate-determining step at the conditions of study (975-1175° K, 1 atm) was H_2 dissociation. This is supported by other studies as well (137).

Similar studies were done by Gardner, et al. (133, 135) at conditions more representative of a typical process (0-1000°C, 0-1000 psig). These high pressure thermobalance studies were used to develop a rough kinetic model in which the activation enthalpy was assumed to be a linear function of the extent of reaction. The salts $KHCO_3$, K_2CO_3, and $ZrCl_2$ were found to be effective catalysts for hydrogasification. In another recent study (136), Ni, Pt, and Rh were found to be very effective catalysts for hydrogasification to CH_4. The reaction occurs in two stages. First, amorphous carbon is quickly gasified. During the course of reaction some carbon graphitizes. The latter does not gasify until higher temperatures are attained.

4. PERSPECTIVE FOR FURTHER RESEARCH

Catalytic carbon and coal gasification is a complex area. Indeed, many of the complexities described in this section are responsible for the slow progress which has been made in understanding the nature of the processes occurring at the catalyst-carbon interface. However, some general trends can be discerned. For the steam gasification reaction, base catalysis is likely to be important for H_2O activation, probably a rate-determining step over a significant range of conditions. Future programs should be directed at understanding this catalytic reaction over a broad range of temperatures and pressures. This would require the use of high pressure thermobalance similar to that used by Gardner and co-workers (133). Correlations between basicity and gasification rates will be useful. These comments apply to the hydrogasification reaction as well. Work in these areas will have to include efforts to characterize the catalyst and the carbon. This admittedly presents some technical challenges, however, it is the only way in which these systems will be more clearly understood.

In terms of a "single-step" gasification to methane in one reactor, techniques must be devised to combine compatible gasification and methanation functions in one catalyst. These functions must also be relatively insensitive to sulfur, nitrogen, and in some instances to mineral matter.

The progress which has been made in catalytic materials over the last decade (see Part 2) will play a major role for catalytic gasification. Increased understanding of the nature of acid and base catalysis in activating hydrocarbons should find relevance for coal gasification. The synthesis of hydrogenation functions which are sulfur insensitive is now possible with the increased understanding of such effects as metal-support interactions. Thermally stable materials which have been developed for catalytic oxidation or automotive catalysis will also find applications. Finally, there are possibilities for the application of novel contacting systems for more effective gasification. These might include molten salt catalysis and gasification at supercritical conditions. All of these possibilities will be developed in Part 2, and described in more detail with respect to coal gasification in Part 3.

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