# IX. ADVANCED SYNTHESIS OF SELECTED FEEDSTOCKS, DIESEL FUEL AND LPG FROM CO AND $H_2$

## A. INTRODUCTION

In Fischer-Tropsch synthesis, hydrogen and carbon monoxide are reacted over a catalyst to produce hydrocarbons with two or more carbon atoms. In contrast to methanation where only one product is desired, it may be desirable to optimize Fischer-Tropsch synthesis to control the selectivity to a variety of hydrocarbon products. For use as chemical feedstocks, ethylene, propylene, benzene, toluene and xylenes are highly desirable. For the production of peak-shaving liquids to be used in a coal gasification-combined-cycle electric power facility, selectivity to a given product is not essential and practically any hydrocarbon liquid fraction ($>C_5$) is acceptable for this use. For the production of motor fuels, isoparaffins in the range of $C_6$ to $C_{10}$, and single-ring aromatics are preferred. As can be seen, significant selectivity control is necessary to produce the extensive range of desired hydrocarbon products. In actual operation, most synthesis schemes produce substantial quantities of less desirable materials, methane for example, or product distributions that are <u>very broad</u> with a significant fraction of the product below or above the required range.

The thermodynamics of hydrocargon synthesis from CO and $H_2$ have been described extensively in the literature (1,2). Review of these data lead to a number of observations important for

Fischer-Tropsch synthesis.

i. All of the reactions forming hydrocarbons from $H_2$ and CO are exothermic so that the free energy of the reaction increases with temperature and the equilibrium constant decreases with temperature.

ii. Reaction to form methane has the most negative free-energy change on a per carbon atom basis.

iii. Below a temperature of $350^0$C, most of the reactions have an equilibrium constant greater than one while above $450^0$C nearly all of the synthesis reactions become thermodynamically unfavorable. The exceptions to these generalizations are methane which has an equilibrium constant for formation from $H_2$ and CO greater than one up to $650^0$C and acetylenic hydrocarbons, especially acetylene and methylacetylene, which have equilibrium constants less than one at temperatures as low as $200^0$C.

iv. The hydrogenation of $CO_2$ to hydrocarbons is thermodynamically more favorable than the hydrogenation of CO.

v. Reactions of CO and $H_2$ with methane to form higher hydrocarbons are thermodynamically feasible.

vi. The formation of olefinic hydrocarbons are slightly less favored than paraffinic materials. Reaction to cyclohexane and methylcyclohexane have equilibrium constants very near those for n-hexane and n-heptane.

vii. The formation of isomeric paraffins are thermodynamically favorable in comparison to normal paraffins.

viii. The free energies of formation of aromatic hydrocarbons, e.g. benzene and toluene, are very close to those of the monoolefins and formation from CO and $H_2$ at temperatures below $400^0$C are possible.

ix.  Alcohols larger than methanol can be produced in substantial quantities at synthesis conditions.

x.  Hydrogenation of olefins and dehydration of alcohols are thermodynamically possible at usual synthesis conditions.  Thus, alcohols must be a primary product while olefins and paraffins may be produced by dehydration of alcohols and hydrogenation of olefins, respectively.

xi.  The equilibrium constant is independent of pressure, however, an increase in operating pressure will increase the conversion of the Fischer-Tropsch reactions as a result of the large volume decrease associated with the synthesis reactions.

The items discussed above demonstrate the possible reactions that can occur during synthesis.  The implications of the thermodynamic observations are that low reaction temperature and increased pressure is preferred in the synthesis of higher hydrocarbons.  Since methane is by far the preferred equilibrium product, kinetic control and selectivity regulates the product distribution.  In general, the product distribution observed during synthesis differs substantially from that which is thermodynamically preferred.  For example, straight chain paraffins and some $\alpha$-olefins represent a large fraction of the hydrocarbons produced.  Few isoparaffins and virtually no cyclic or aromatic materials are produced.  Similarly, CO is preferentially hydrogenated due to its stronger interaction with the surface, and $CO_2$ reacts only after most of the CO has been removed.

The general Fischer-Tropsch reactions for paraffin formation can be written as

$$(2n+1)H_2 + nCO \longrightarrow C_nH_{2n+2} + nH_2O \qquad (IX-1)$$
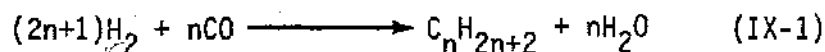
in which water is the oxygenated product, or when $CO_2$ is the oxygenated product, the reactions are

$$(n+1)H_2 + 2nCO \longrightarrow CnH_{2n+2} + nCO_2 \qquad (IX-2)$$
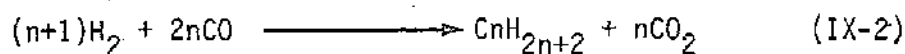
Similar reactions can be written for olefins, aromatics, cycloalkanes, and alcohol production. The ratio of $H_2$ to CO consumed in these reactions is 2 when water is produced and 0.5 when $CO_2$ is produced. In general, at low temperatures usually employed in the synthesis reaction, water is the primary product and $CO_2$ is a secondary product formed as a result of the water-gas shift reaction. This reaction is slow at the temperatures and over the conventional catalysts employed in Fischer-Tropsch synthesis. The ratio of $H_2$ to CO required in the feed to the synthesis catalyst is approximately 2, but this should not be considered as a firmly set parameter since varying the $H_2$/CO ratio may have an important effect on the product distribution.

Table VII-1, presented in Section VII of Part 3, lists the product composition of a number of gasification processes. The $H_2$/CO ratio in the synthesis gas varies from 0.55 to 3.2 with most of the processes producing gas with a ratio of approximately 2. As discussed in Section VII, ratios below the desired value can be increased through the water-gas shift reaction, therefore, no constraints should exist with respect to feed gas composition.

Thus, the problem of Fischer-Tropsch synthesis becomes one of catalytic selectivity as well as activity and activity maintenance. As mentioned earlier, a number of different hydrocarbon fractions may be preferred with the optimum situation represented by a relatively

narrow product distribution or alternatively a large fraction of a specific chemical in the product stream.

B.  SUMMARY OF MAJOR PROBLEM AREAS AND CATALYST DEVELOPMENT OBJECTIVES

In the following section, recent data from pilot and bench scale catalyst tests and data from an operating Fischer-Tropsch plant, (Sasol, South Africa) will be analyzed to illustrate current catalyst capabilities and shortcomings.  Hydrocarbon synthesis catalysts suffer from many of the same problems previously discussed for methanation.  Activity maintenance affected mainly by sulfur poisoning, carbon deposition, and thermal degradation of the catalyst is a major problem.  However, product selectivity and the factors that influence product selectivity are important as well.  High activity is also desirable since low temperature operation appears to be necessary for optimum selectivity.

Numerous bench and pilot plant scale tests of the Fischer-Tropsch synthesis have been conducted and most of these data are available in the literature.  Much of the older work was done with iron and cobalt catalysts containing a variety of promoters.  The effects of temperature, pressure, reaction time (space velocity), $H_2/CO$ ratio , and sulfur level were studied.  Product selectivity was reported mainly as distillation fractions, i.e. methane or gaseous fraction, LPG ($C_2$ to $C_4$), and several distillation fractions.  In some cases, water soluble organics were also measured separately.  The lack of reliable activity-selectivity data for specific products was due primarily to the unavailability of modern chromatographic and mass spectrometer instrumentation which are necessary for complete and rapid analysis.

More recent data generally report results for specific products from methane to $C_6$ or higher including alkenes, alcohols, and some isoparaffins. Reliable product analysis is important not only in the testing of fresh catalysts, but also in assessing degradation since selectivity may change substantially.

1. SELECTIVITY

An early catalyst system that was optimized to give good activity and selectivity were supported cobalt catalysts with approximate compositions of 100 Co : 18 $ThO_2$ : 200 kieselguhr and 100 Co : 5 $ThO_2$ : 10 MgO : 200 kieselguhr. An extensive review of the product composition from a variety of catalytic materials is given by Anderson (3) who also discusses the effects of promoters and process variables. A typical product distribution is that presented in Figure IX-1 obtained for a supported cobalt catalyst at the following conditions (4):

| | |
|---|---|
| Catalyst | 100 Co : 18 $ThO_2$ : 100 kieselguhr |
| Temperature | $190^{\circ}$C |
| Space velocity | 100 $hr^{-1}$ |
| $H_2$/CO | 2/1 |
| Pressure | 1 atm |

Other factors that influence the product distribution for such Co catalysts are:

i. At low temperatures, 160 to $175^{\circ}$C, and low conversion of CO and $H_2$, a significant fraction of the product was oxygenated hydrocarbons, predominantly alcohols.
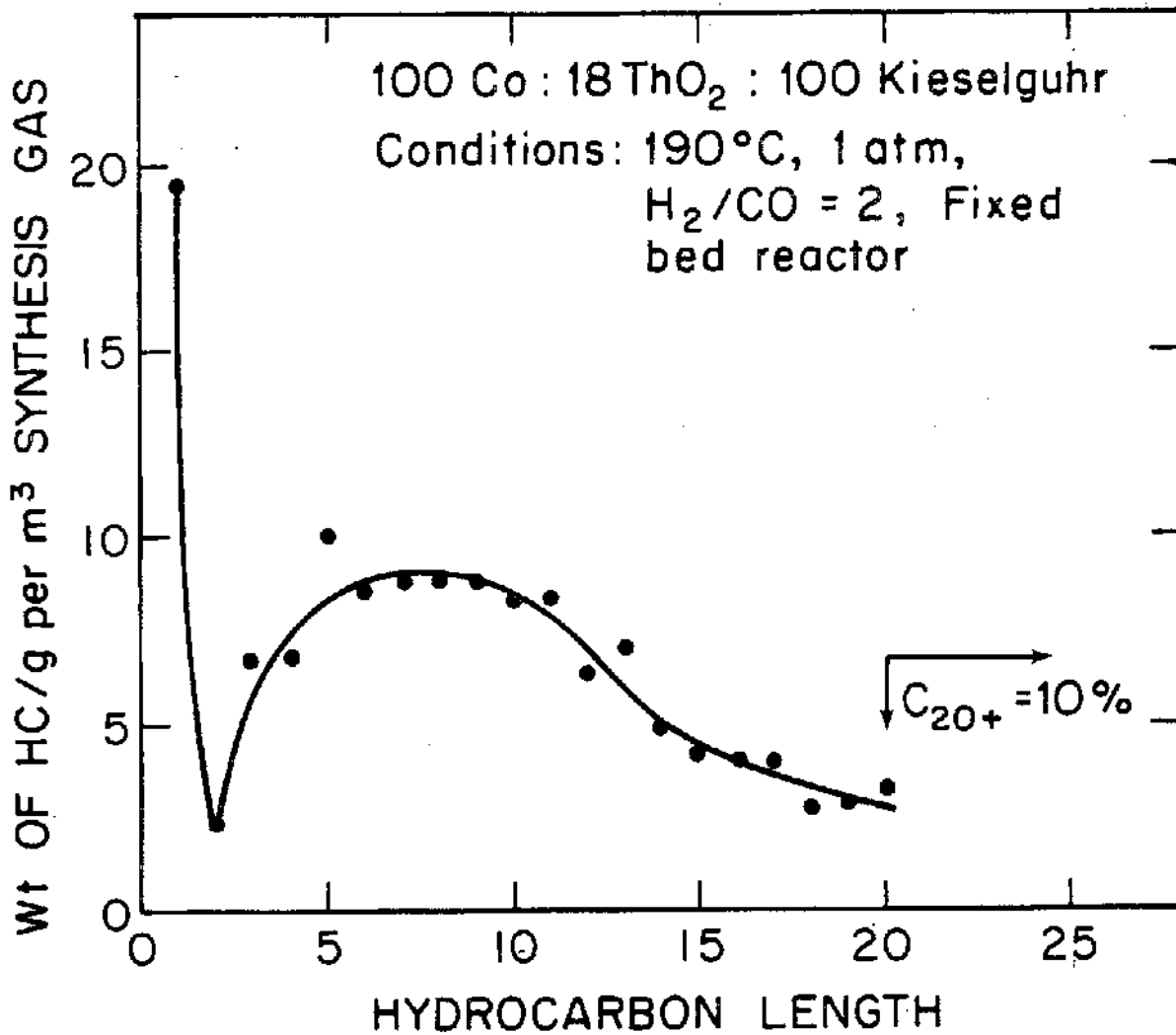
521

Figure IX-1.     Synthesis Product Distribution From
                 a Co/ThO$_2$/Kreselguhr Catalyst (Ref. 4)

ii.  At $190^\circ$C, the fraction of alcohols was very small.

iii.  The olefin content varied from $\sim$ 25% at $C_5$ to 10% at $C_{10}$, and continued to decrease as the chain length increased.

iv.  Operation at higher pressures, 5-15 atm, shifted the product distribution to higher molecular weights, decreased the olefin content, and increased the fraction of wax ($> C_{18}$).

v.  Promoters such as thoria and potassium carbonate had only a small effect on the selectivity.  Thoria, however, increased the activity of Co catalysts permitting the use of lower temperatures with a greatly preferred product distribution.

vi.  Increasing the temperature decreased the average molecular weight of the products and increased the fraction of gaseous products, especially methane.

vii.  Decreasing the $H_2$/CO ratio from 2 to 1 greatly increased the olefin content, increased the molecular weight and also increased the alcohol production.  The ratio of $H_2$ to CO consumed remained near 2.

It should be noted that the effect of pressure, temperature, and $H_2$/CO ratio is generally similar on most catalysts.

The second example is a fused iron catalyst operated in a fixed bed reactor with gas recycle (Synol Process) (5), a process optimized to produce oxygenated products.

| | |
|---|---|
| Catalysts | $Fe_3O_4$/$Al_2O_3$/$K_2O$  (fused iron) |
| Reactor | Packed Bed |
| $H_2$/CO ratio | 1.3/1 |
| Space velocity | 250 $hr^{-1}$ |
| Pressure | 20 atm |

Temperature        190 to 210°C
Recycle ratio      10

The carbon number distribution is presented in Figure IX-2. Some observations that can be made for this catalyst are:

i.  Operation of iron catalysts at atmospheric pressure generally result in poor activity, short life, and a product distribution skewed to low carbon number.

ii.  Alcohols are produced, and persist up to high carbon number and represent a relatively large fraction of the total product.

iii.  The olefin fraction is also very large.

iv.  Compared with Co catalysts, the product distribution from iron has a sharper maximum which appears at lower carbon number.

v.  Iron also gives more highly branched hydrocarbons and larger fractions of olefins and oxygenated molecules.

vi.  The relatively large fraction of high molecular weight materials, $C_{17+}$, is not a general property of Fe catalysts.

A second Fe catalyst for which a large body of very detailed data is available is a test done in the early 1950's using iron in a fluidized bed reactor (6).

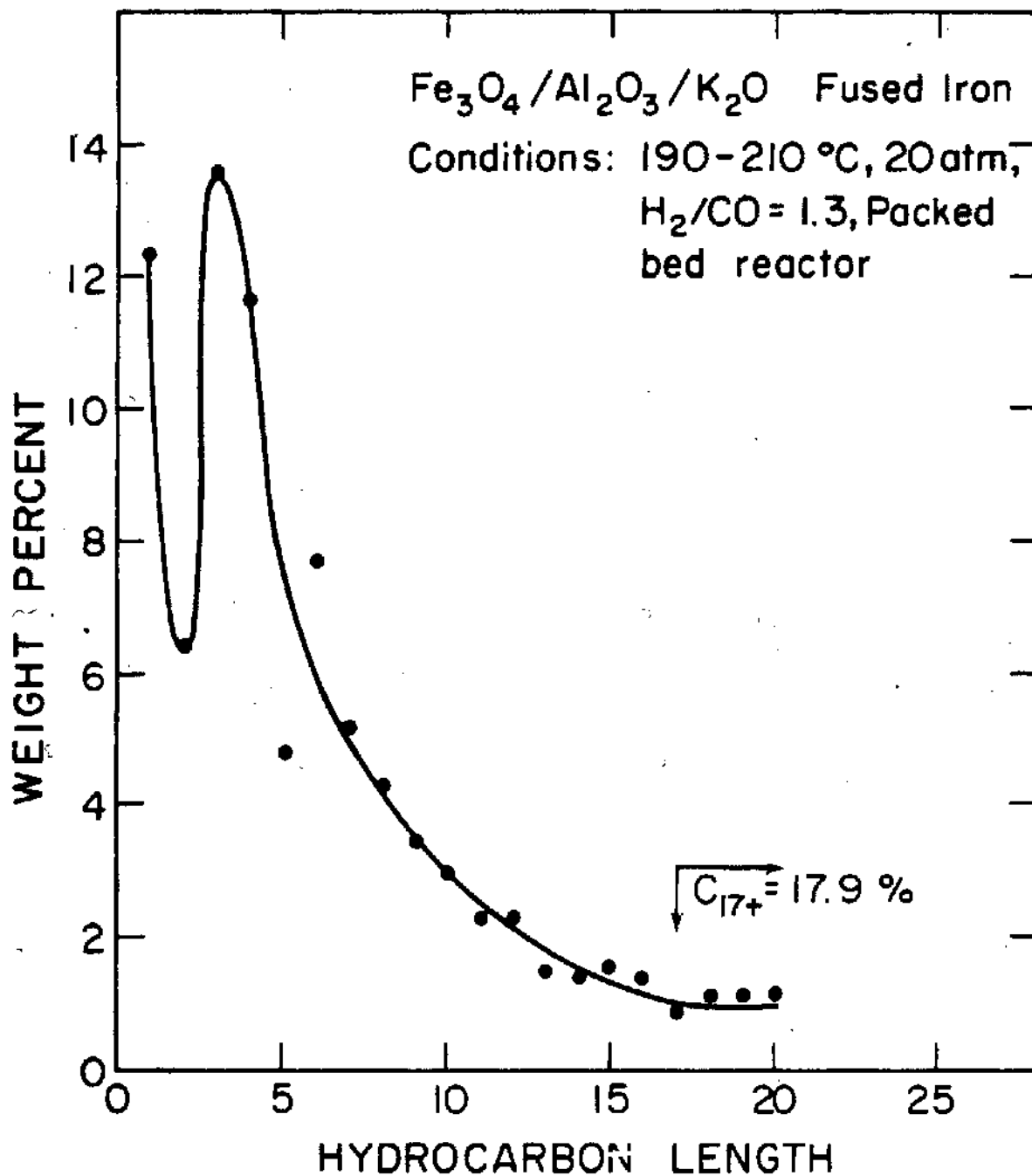| | |
|---|---|
| Catalyst | $K_2CO_3$ Promoted Iron Oxide (reduced before use) |
| Reactor | Fluidized Bed |
| Temperature | 315°C |
| Pressure | 18 atm |
| $H_2$/CO ratio | 2/1 |
| Space velocity | 700 hr$^{-1}$ |
| Recycle ratio | 2 |

Figure IX-2.    Synthesis Product Distribution From
                Promoted Fused Iron Catalyst (Ref. 5)

The product distribution by carbon number is given in Figure IX-3.
These data indicate that:

i. In spite of the high temperature, $315^{\circ}C$, the fraction of
methane is relatively low and the product distribution is somewhat
broader than that in Figure IX-2 for fixed bed synthesis.

ii. A large fraction of the products are oxygenated, 27%
of the total products containing oxygen.

iii. A relatively large proportion of the products are olefins,
especially at low carbon number. The olefin content is clearly
shown to be a function of alkali content; catalysts containing
no alkali produce very little olefinic material.

iv. The fraction of long chain hydrocarbons ($C_{17+}$) is much
smaller in the fluid bed synthesis at $315^{\circ}C$ than in the fixed
synthesis at $200^{\circ}C$.

These data represent only a small fraction of that available
for Co, Ni, and Fe catalysts with numerous promoters and under a
variety of conditions. A variety of reactor types have been tried
including recirculating oil (1), hot gas recycle (8), and the
fluidized bed reactors mentioned earlier. These investigations
were directed at achieving close temperature control to maintain
product selectivity. The reviews of Anderson (1) and Storch et. al.
(2) cover much of the earlier work, and Pichler and Schulz (7a)
and Eidus (7b) most of the intervening work. The number
of possible additives and reaction conditions that affect the
operation of the catalyst make the system extremely complicated and
at present not well understood. For example, the only commercial
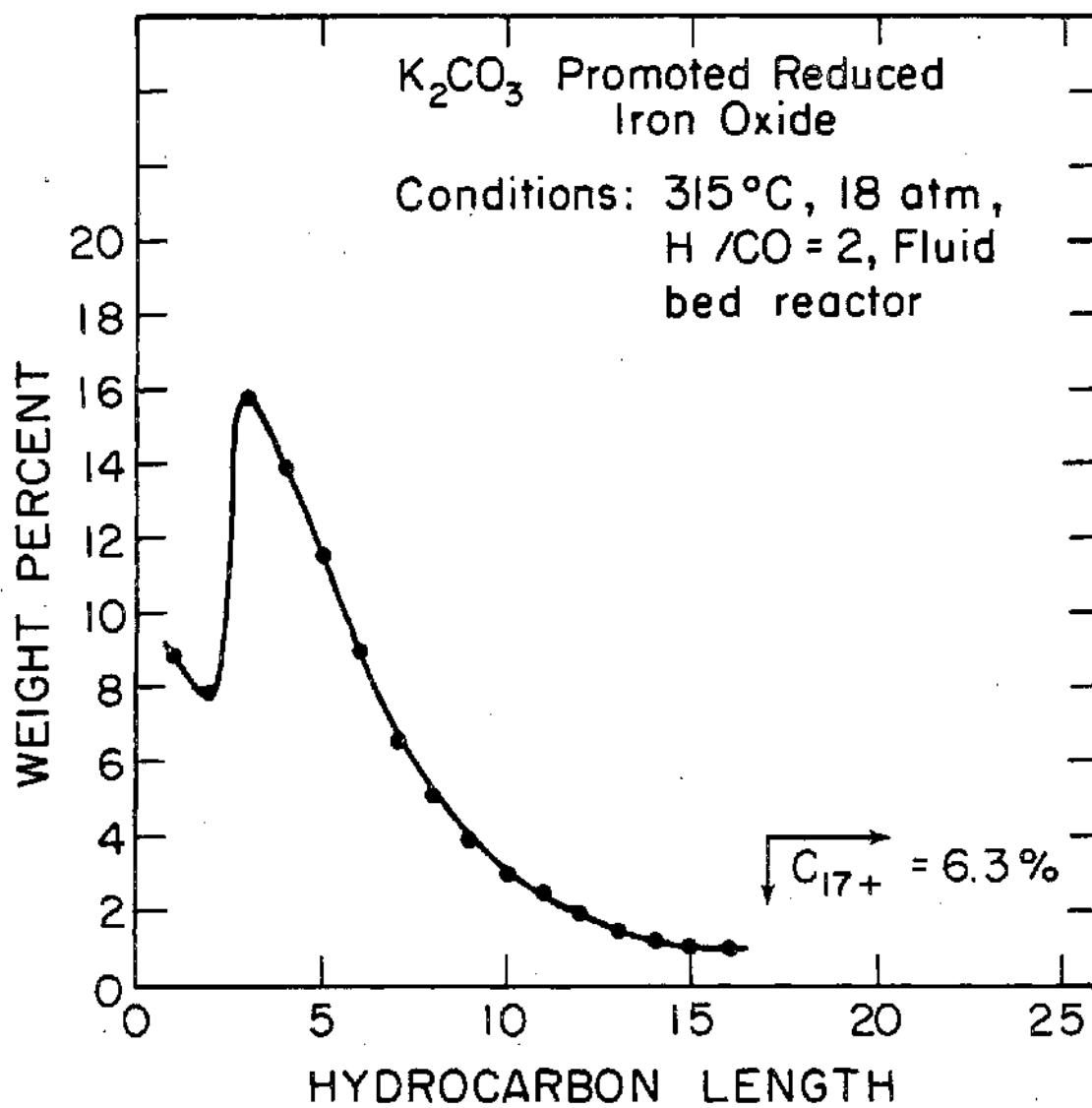
Figure IX-3.    Synthesis Product Distribution From Promoted
                Iron Oxide in a Fluid Bed Reactor (Ref. 6)

527

plant in operation at Sasolburg, South Africa, is optimized for the production of liquid hydrocarbons. However, the fluidized bed Synthol reactors currently in use produce 14% methane and the $C_1 + C_2$ fraction represents 27% of the total hydrocarbon production (7). The product distribution is considered quite good with the useful hydrocarbon fraction, defined as $C_{3+}$, representing 64% of the products with the very heavy hydrocarbons (wax) very small due to the operating temperature and the recirculating catalyst. Further tightening of the product distribution will require a greater understanding of the reacting system.

In Part 1 of this study, the reaction mechanism of hydrocarbon synthesis was discussed in detail. Basically, the mechanism is the same as that for methane synthesis with the additional step of polymerization of the hydrocarbon surface intermediates to produce liquid hydrocarbons. The hydrocarbon chain length is determined by a competition between the polymerization of $H_2COH$ surface species and the hydrogenation and desorption of the surface polymer in a termination step. An alternate mechanism consistent with homogeneous reaction processes is the repeated insertion of CO into a surface hydrocarbon residue. Either mechanism is consistent with many of the observed effects of catalyst composition and process variables on product selectivity. For example:

i. Alteration of the catalyst to affect the relative binding of CO and $H_2$ will change the surface coverage of the surface complex and the probability of subsequent carbon addition. Indeed, promoters such as $K_2O$ which are strong bases have been shown to shift the hydrocarbon

distribution to longer chain length. Potassium oxide is thought to donate electrons to the metal resulting in a strenthening of the M-CO bond, and, therefore, weakening the C≡O bond.

ii. Metals with lower hydrogenation activity generally give higher molecular weight product distributions and larger proportions of olefins. In the latter case, very weak hydrogenation activity may actually result in the hydrocarbon leaving the surface by dehydration of the alcoholic intermediate to an olefin.

iii. A change in $H_2/CO$ ratio results in a direct change in surface composition of adsorbed $H_2$ and CO and the resulting product distribution.

Besides study of a variety of promoters and some work on the effect of the support on the resulting product stream, the area of catalyst composition and its effect on product distribution is relatively unstudied. This will be considered in more detail later.

2.    SULFUR POISONING

Conventional synthesis catalysts are highly sensitive to sulfur poisoning at very low levels of sulfur. The interaction of $H_2S$ with the catalyst is similar to that encountered in methanation with nearly quantitative uptake of the sulfur and complete deactivation of the catalyst. Karn and co-workers (9) studied the sulfur poisoning of several iron catalysts in a bench scale test at high pressure and high conversion. Very low sulfur levels, in the range of 5 to 50 ppm $H_2S$, lead to very rapid deactivation of the catalyst. The deactivation was approximately linear with sulfur added and approached zero activity at catalyst sulfur levels approaching one monolayer. These data, collected in Table IX-1,

## TABLE IX-1

## SULFUR POISONING OF Fe CATALYSTS (a)

| Catalyst | $H_2S$ Feed (ppm) | Catalyst (b) S Level (MgS/g cat) | S Monolayer (c) Area ($m^2/g$) | Measured Catalyst Surface Area ($m^2/g$) |
|---|---|---|---|---|
| Fused Promoted Iron (Fe/Mg/Cr/K) | 4.5 | 0.33 | 0.50 | 0.9 |
| Promoted Iron Turnings (Fe/K) | 46 | 0.28 | 0.42 | 0.6 |

(a)  Data from reference (9).

(b)  Catalyst S content obtained by extrapolation to zero activity.

(c)  Calculated assuming $8\overset{o}{A}^2$ per sulfur atom.

show quite clearly that the sulfur required to deactivate the catalyst must only be sufficient to cover the available catalyst surface area. Most of the sulfur fed to the reactor is retained by the catalyst even at higher feed levels (50 ppm $H_2S$) and higher operating temperatures ($350^o C$) (10). For the catalysts considered in Table IX-1, massive iron materials, the surface area is predominantly reduced iron. At sulfur levels of 15 ppm, complete poisoning corresponds to only 100 hrs. of operation implying a limited catalyst life unless the feed sulfur level is decreased to extremely low levels, 0.1 to 0.01 ppm $H_2S$. This has been discussed in detail in Section VII of this report (11).

Product selectivity also changes as the catalyst is poisoned by sulfur. Increased methane production is observed on promoted iron extensively deactivated by sulfur addition (9) Herington and Woodward (12) observed that sulfur addition to a thoria-promoted-cobalt catalyst first increased the liquid hydrocarbon yield, then with more extensive poisoning shifted the product distribution to gaseous hydrocarbons, and similar results are reported for Ni and promoted Ni catalysts (13). Craxford attributed the initial shift in product distribution toward liquid hydrocarbons to the poisoning of the hydrocracking function of the catalyst (14). Herington and Woodward attribute the effect to a preferential poisoning of the surface hydrogenation function, thus, leading to longer hydrocarbons due to increased polymerization (12).

An additional problem, as a result of sulfur poisoning, is that a partially deactivated catalyst cannot be operated at higher

531

temperature to maintain conversion. Such temperature increases will adversely affect the product distribution, and if the temperature is sufficiently high, will cause carbon deposition and plugging of the catalyst bed.
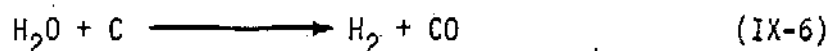
### 3. CARBON DEPOSITION

The disproportionation of CO to $CO_2$ (Boudouard Reaction) and carbon leads to another major problem area.

$$2CO \longrightarrow CO_2 + C \qquad (IX-3)$$
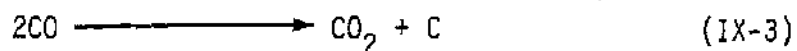
The deposition of carbon can lead to catalyst deactivation, destruction of the catalyst pellet and increased attrition and physical plugging of the reactor. As discussed in Part 3, Section VII of this report (15), the conditions under which carbon formation is thermodynamically permitted are well defined. The ternary diagram of White et. al. (16) is a particularly useful presentation format and permits a rapid assessment of whether carbon deposition is thermodynamically favored. However, as cautioned in Section VII, the involvement of such gaseous species as $H_2$ and $H_2O$ occur through the reactions

$$H_2O + CO \longrightarrow H_2 + CO_2 \qquad (IX-4)$$
$$3H_2 + CO \longrightarrow H_2O + CH_4 \qquad (IX-5)$$
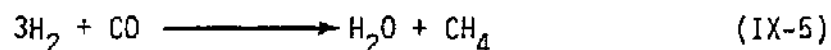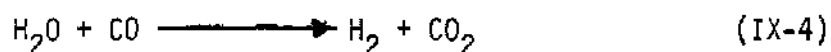
or alternatively the steam gasification of carbon.

$$H_2O + C \longrightarrow H_2 + CO \qquad (IX-6)$$

At conditions where kinetic limitations prevent these reactions from proceeding to equilibrium, the above described thermodynamic predictions became tenuous.

At the usual conditions employed in Fischer-Tropsch synthesis, i.e., an $H_2/CO$ ratio less than 2, pressures of 1 to 50 atmospheres, and temperatures below $350^{\circ}C$, carbon is thermodynamically stable (17). However, it is generally found that very little carbon is deposited on most synthesis catalysts. This is true for Fe, Ni, and Co materials at temperatures below approximately $300^{\circ}C$. As the temperature is raised above this limit, carbon deposition has been observed to occur on iron lathe turnings (18) and on sulfur-poisoned-fused-iron catalysts (9). The lack of carbon deposition is a result of the low temperatures employed and the low rate of the Boudouard Reaction on these catalysts.

4.    ACTIVITY MAINTENANCE

In addition to the areas of sulfur poisoning and massive carbon deposition discussed above, numerous other mechanisms exist which result in degradation of catalyst performance. Such processes are due to a variety of physical or chemical changes in the catalyst, adsorption of high molecular weight products on the catalyst, and attrition. In the synthesis of hydrocarbons, even nominally degraded activity can be especially important since the selectivity may be adversely affected or an increase in temperature to maintain reaction rate can also alter the product distribution in a negative manner.

This is exemplified by the commercial operation at Sasol, South Africa, where promoted iron is used as a catalyst and generally replaced after approximately 50 days (19). The synthesis gas is cleaned of sulfur to very low levels, 0.01 ppm, and should

not cause significant problems. However, in use, the catalyst
deteriorates and the temperature is raised to maintain a constant
synthesis rate. The higher operating temperature results in a
change in product distribution toward lower carbon numbers, and
catalyst life becomes a trade off between catalyst replacement
cost and the poor product selectivity. Pichler considers the
same phenomenon with Co catalysts that show a slow deterioration
with time (7). This is partly due to sulfide and sulfate formation,
but carbon deposition and sintering were also observed. These
latter phenomena were attributed to inadequate control of the
reaction heat.

5.   SYNTHESIS OF DIESEL FUEL AND LPG

Uses for which the Fischer-Tropsch product is better
suited are diesel fuel, jet fuel, and liquified petroleum gas (LPG).
These particular materials have recently received attention due to
their national importance (20). The properties and chemical
composition of these materials will be briefly described below
before a comparison is made with the products of hydrocarbon synthesis
processes.

The properties and composition of diesel fuel was reviewed
in Part 3, Section II (21). Diesel fuel is a middle-distillate-
hydrocarbon fraction whose important ignition properties are
characterized by the cetane number, equal to 100 for cetane
(n-hexadecane) and 0 for $\alpha$-methyl-naphthalene. Cetane numbers
are usually in the range of 35 to 50, paraffinic fuels having
better ignition characteristics. Aromatics and multi-ring aromatics
are to a certain extent undesirable since they lead to smoke

534

formation, carbon formation and excessive "knocking". Boiling range of the fuel can vary from 325-550°F to 350-800°F and the sulfur level can be as high as 1.2% depending on application.

Jet fuels are similar to diesel fuels in that high paraffin content is preferred. Important properties are:

i. high energy content per unit weight making paraffins with a high hydrogen to carbon ratio highly desirable;

ii. very low level ( <3%) multi-ring aromatics since these cause carbon deposition and resulting engine wear as well as smoke; and

iii. a low sulfur level, 0.1 to 0.4%, due to possible corrosion of engine parts.

Liquified petroleum gas has a simple composition consisting essentially of $C_3$ and $C_4$ hydrocarbons. It is, in fact, sold in many cases as butane or propane with minimum concentrations of the major component specified. This composition gives LPG a very high energy content compared to methane, 2500 BTU/Ft$^3$ for propane and 3200 BTU/Ft$^3$ for butane, making this material very useful as an exceptionally clean fuel in mobile equipment (octane number of 100) as well as a storable replacement for natural gas. Depending on use, the sulfur content is generally low.

In this general class of fuels and especially for diesel fuel, the preferred components are paraffinic hydrocarbons, mainly normal paraffins with some branched chain components desirable to control physical properties. These are just the materials produced by the low temperature Fischer-Tropsch synthesis as practiced over promoted iron and cobalt catalysts. The product distribution for a

typical cobalt catalyst presented in Figure VIII-1 shows a broad maximum from $C_4$ to $C_{15}$. This is somewhat low for diesel fuel where the distillation range of 325 to 800°F specifies a hydrocarbon composition extending from approximately $C_9$ to $C_{25}$. Thus, much of the synthesis products are below the desired range. A lighter distillation fraction such as kerosene for use as a jet fuel has a distillation range of 300 to 500°F and corresponding composition in the vicinity of $C_9$ to $C_{16}$. This more closely corresponds to that found in Figure IX-1. However, the major · point is that the chemical form of the synthesis products under certain operating conditions can be used for this class of fuels with minimum subsequent treatment. The broad range of paraffinic hydrocarbons together with a small fraction of ∝-olefins and branched chain hydrocarbon may only require a simple hydrogenation step and distillation. If the heavier diesel fuel fraction is wanted, a shift in the product distribution to higher molecular weights would be required. Alternately, the product distribution obtained from the fused-promoted-iron catalyst (Figure IX-2) has a maximum of $C_3$ and $C_4$ material, necessary for LPG. However, a majority of the total product is outside of this range.

## C. RESEARCH AND DEVELOPMENT AREAS PERTINENT TO FISCHER-TROPSCH SYNTHESIS

Application of the developments presented in Parts 1 and 2 of this study, which are pertinent to the solution of problems encountered in the synthesis of hydrocarbon fuels and chemicals from CO and $H_2$, will be considered here. These may overlap somewhat

with the discussions of water-gas shift and methanation in Section VI, however, in general, the approach will be quite different mainly due to the importance of selectivity in Fischer-Tropsch synthesis. The discussion is divided into three areas as in previous sections; short-term, long-term, and basic research and development efforts.

1. SHORT-TERM PROGRAMS

a. Examination of Common Catalytic Materials

In the search for catalysts with product distributions, emphasizing liquid hydrocarbons or specific chemicals, a variety of catalytic materials must be evaluated for activity and selectivity. The major portion of past work was concerned with Co, Fe, Ni, and to a smaller extent with Ru and combinations of these metals with a variety of promoters. The noble metals, Pt, Pd, etc., have not been examined in detail under a variety of conditions for synthesis rate and selectivity. One example which shows the possible advantages of these materials, is the use of alumina supported Pt to produce large fractions of ethane and dimethyl ether reported recently by Vannice (22). At atmospheric pressure and with a $H_2/CO$ ratio of 2, Pt shows very high selectivity to methane (23). However, at lower $H_2/CO$ ratios, and especially at higher pressures, the production of ethane increases. As the pressure is raised to 10 atmospheres or higher, the fraction of dimethyl ether increases dramatically. Representative data illustrating these effects are collected in Table IX-2. Although platinum had been examined previously for the synthesis reaction, the proper combination of $H_2/CO$ ratio and pressure are required for the product distribution found. It should

# TABLE IX-2

## SYNTHESIS OF ETHANE, ETHYLENE AND DIMETHYL ETHER ON $Pt/Al_2O_3$

| Temp. ($^{\circ}C$) | Pressure (atm) | $H_2CO$ Ratio | Product Distribution (mole percent) | | | |
|---|---|---|---|---|---|---|
| | | | $C_1$ | $C_2$ | $C_3$ | DME* |
| 280 | 1.0 | 2 | 90+ | 5 | 0 | 0 |
| 271 | 1.0 | 0.5 | 82 | 19 | 0 | 0 |
| 263 | 1.96 | 1 | 89 | 12 | 0 | 0 |
| 271 | 2.12 | 1 | 85 | 10 | 0 | 5 |
| 274 | 10.1 | 1 | 70 | 8 | 0 | 23 |
| 269 | 30.0 | 1 | 67 | 4 | 0 | 30 |

Ref. (22) and (23).

\* Dimethyl ether

also be noted that the support was found to be important, although no data on this aspect was given.

The data presented above emphasize the importance of the reaction conditions, especially $H_2/CO$ ratio and total pressure, in controlling product distribution. Although most common catalytic materials have been examined for $CO-H_2$ synthesis in one form or another, the systematic investigation of a variety of these materials may provide useful leads on catalyst properties necessary for the production of specific chemicals. Changes in activity and selectivity with time should also be investigated since changes in the bulk or surface composition of the catalytic phase during synthesis is the rule rather than the exception.

As previously discussed, the support is an important aspect of the supported metal catalyst system, and should also be examined. As discussed later, the design of a bifunctional catalyst system with, for example, a hydrogenation component and an isomerization component may be a promising route to various chemicals and valuable fuels. The importance of the support in stabilizing highly dispersed supported metals, and in modifying the properties of the metal through metal-support interaction has been reviewed extensively in Parts 1 and 2.

Other catalytic materials of interest for controlling the activity, selectivity, and activity maintenance properties of catalysts for Fischer-Tropsch reactions include bimetallic alloys or clusters. The properties of these materials are now better understood than several years ago, and modern spectroscopic and

adsorption techniques permit one to fully characterize the surface and bulk chemical and physical properties of these systems. These catalysts are of primary interest because by addition of one metal to another, one can in principle, control various catalytic properties over very extensive ranges. One group of bimetallic catalysts which have been widely studied and are of particular interest for synthesis reactions involves a combination of Groups VIII (e.g. Rh, Ru, Ir and Ni), and IB (Cu, Ag or Au) metals. These combinations enable one to control hydrogenolysis and hydrogenation activity among other parameters (24). It is just these catalytic properties that are felt to be important in controlling Fischer-Tropsch selectivity. The behavior of these materials and the surface composition of the catalytic phase is fairly well understood and extension to hydrocarbon synthesis would be straightforward.

b. Poison Resistant Catalysts

As discussed previously, the need to remove sulfur to the new low levels required by many hydrocarbon synthesis catalysts, 0.1 ppm, increases the cost of the products and reduces the efficiency at which the process can operate. The existence of a catalyst capable of operating in a feedstream with higher levels of sulfur, 10 to 100 ppm, would be advantageous since the end use of the hydrocarbon products can, in most cases, tolerate this and even higher levels of sulfur. The problem in the present case is much more complicated and difficult than that encountered with methanation where use is made of the high thermodynamic stability of methane combined with high operating temperatures to control

selectivity. Hydrocarbon synthesis catalysts are optimized to give a desired product distribution, and introduction of sulfur into the system will adversely alter the selectivity.

However, controlled sulfur poisoning can be beneficial to selectivity by shifting the product distribution toward higher hydrocarbons and decreasing the production of methane as discussed earlier (9, 12, 13), and as shown recently for nickel methanation catalysts (25). The mechanism of operation is thought to be a poisoning of the surface hydrogenation and hydrogenolysis activity leading to an increased hydrocarbon chain length. Of course, if the effect of sulfur can be moderated, the very large decrease in total activity can be controlled. The number of materials that have been examined for product distribution in a sulfur containing stream are few and an effort should be established to obtain such information on a variety of materials.

The number of systems that can be considered in this respect is very large, but some selection is possible. The materials normally considered as catalysts for hydrocarbon production, Fe, Co, Ni and the various promoted mixtures of these should be tested initially, if only to establish a baseline. A systematic study of the important operational parameters on several representative materials, including variation in the level of $H_2S$, should provide an adequate background. Detailed product analysis would be necessary to permit an assessment of changes in product selectivity.

Materials normally not considered good catalysts should

then be examined. The deactivating and selectivity moderating properties of sulfur could have beneficial effects on the catalytic characteristics of some materials (26). Platinum, for example, is thought to bind CO too strongly leading to a low activity (27), and is a good hydrogenation catalyst resulting in a high selectivity to methane. Sulfur poisoning will certainly affect both of these properties, however, the resulting activity and product distribution can be obtained only by experiment. Platinum is also much less susceptible to bulk sulfidation than Fe, Co, or Ni (28). The level of $H_2S$ in $H_2$ required to form bulk PtS is 20 times higher than that needed to form FeS at 700K. Similar differences in the stability of the surface sulfide also exist (26). An extreme example is copper, where the level of $H_2S$ required to form a bulk sulfide is calculated to be 73%, 1000 times higher than that for Fe. The application of controlled sulfidation to bimetallic systems further extends the possibilities for controlling catalytic properties.

The use of zeolites as supports to impart sulfur resistance is also receiving attention recently. Resistance of cracking catalysts to $NH_3$ and $H_2S$ is enhanced compared to amorphous silica-alumina. More interesting, however, is the sulfur resistance imparted to a metal through metal-zeolite interaction. Data indicating an increased resistance to sulfur poisoning has been reported for isomerization and hydrogenation reactions (29, 30, 31). In some of this work, the sulfur level was quite high, up to 0.5% $H_2S$ by volume. The effect is attributed to an electron transfer from the

metal crystallites within the supercage to the zeolite lattice. This may also affect the selectivity during hydrocarbon synthesis.

Supported metal alloys and bimetallic and multimetallic clusters, discussed extensively in Part 1 (32), is another area which may impact on sulfur resistant catalysts. Much work currently in progress is concerned with the effects of alloying on selectivity and activity. However, few results have appeared where sulfur resistance was specifically studied. Little is known of the behavior of such systems in sulfur-free or sulfur-containing systems, however, as discussed in Part 1, the mechanism of sulfur poisoning at levels of 1 to 100 ppm $H_2S$ is probably a competition with the reactants for adsorption sites (26). The formation of a surface sulfide may be strongly affected by addition of a second component to the catalytic metal. Strong compound formation may inhibit formation of a surface sulfide or if the second component is strongly electron withdrawing, the active metal may be more sulfur resistant as speculated for the sulfur resistance of Pt/zeolite catalysts (33). Activity and selectivity data for copper alloyed with other active metals such as Ni would be of great interest as a result of the small tendency of Cu to form a bulk sulfide.

2.  LONG-TERM RESEARCH AND DEVELOPMENT

    a.  New Catalytic Materials

The possibility of finding unusual catalytic properties in the wide variety of new material available from recent research in inorganic and organometallic chemistry, materials science, and

surface science makes such an evaluation worthwhile although long-term in nature. However, the large number of possible materials that could be tested make a systematic approach very important. Ideally, a firm knowledge of the mechanism of hydrocarbon synthesis would be of great use in such an analysis of new catalytic materials, but the absence of such detailed chemical knowledge even on very simple systems (34) makes this an important aspect of supporting research that will be discussed later. Concurrent pursuit of basic mechanistic studies should be of great help in evaluating new materials.

The desired catalytic properties would preferably relate to <u>selectivity and poison resistance.</u> Activity would not be a primary concern initially. Considering selectivity first, the major problem with current processes is the lack of control on the product distribution. As the data presented earlier indicate, product distributions achieved in hydrocarbon synthesis tend to be broad with a pronounced maximum at methane. The $C_{2+}$ hydrocarbons have a narrow maximum at $C_4$ to $C_6$ or a broad maximum extending from $C_3$ to $C_{12}$, and the specific hydrocarbons produced are normal parafins or $\alpha$-olefins. Such materials are chemically not very useful as transportation fuels because of their low octane quality. The production of high octane hydrocarbon materials such as isoparaffins or aromatics, the latter also being a valuable chemical feedstock, is thermodynamically possible. The heats of formation of aromatics are similar to those of the corresponding monoolefins, and not significantly different from the heats of formation of normal paraffins from CO and $H_2$. These data can be

viewed in two ways. First, except for methane, there is no clear thermodynamic driving force for the production of specific hydrocarbons including isoparaffins and aromatics of interest here. Alternatively, one can view catalyst selectivity as the controlling factor for the production of specific chemicals, a variety of which are thermodynamically possible. The possibility of the latter will be clear only when highly specific catalysts become available. Some examples that approach this required selectivity will be described in the next section.

Hydrocarbon synthesis catalysts require both hydrogenation activity and polymerization or CO insertion activity necessary for chain building. As previously mentioned, alloy formation or multimetallic cluster formation is a promising route to alter the catalytic properties of a metal surface. Some systematic understanding of the surface properties of alloys is emerging from recent work on a variety of metals and reactions. However, a detailed evaluation of the application of alloy systems to hydrocarbon synthesis is a long-term research effort. The approach taken by Sinfelt and co-workers to the development of petroleum reforming catalysts is a good example (24). This group began with the determination of the specific activity of a broad range of supported metals for several model reactions. This was a necessary first step since it permitted some understanding of the metal properties important to the class of reactions of interest. A self-consistent model relating the reaction kinetics from one metal to another also resulted from this work. At this point, combinations of metals were tested where the choice of each

545

component was made to either enhance or inhibit one part of the catalytic process. In the case of hydrocarbon synthesis, Vannice has measured the specific activities of all the Group VIII metals at atmospheric pressure and several $H_2/CO$ ratios (23). This may be adequate although data at lower $H_2CO$ ratios, 1 to 2, and higher pressures may be more useful since pressure can have a large effect on product distribution in this reaction. Subsequent work on other metals, especially those of Group IB and then the study of well charactierized alloy systems would be of interest.

Some preliminary work on several alloy systems shows a definite effect of composition on selectivity. Some of these investigations were directed primarily at methanation, utilizing high $H_2/CO$ ratios, and therefore, are of limited use in the present context, while others are directed toward $C_{2+}$ hydrocarbon synthesis. Bartholomew recently reported preliminary results comparing supported Ni and Ni combined with Mo, Co, Pt, Ru, Rh, and Pd (35). Since the noble metals have a much higher selectivity to methane, it is not surprising that $Ni-Pt/Al_2O_3$ catalysts show very high selectivity to $CH_4$ while addition of Co or Ru depresses slightly the production of $CH_4$. The effects of alloying may be magnified by the use of conditions more appropriate to the synthesis of higher hydrocarbons. Second, an investigation of Pt-Fe alloys using Mossbauer spectroscopy to characterize the state of the iron, shows that when Fe is alloyed with Pt, it loses its activity for synthesis and shifts the product distribution to lower molecular weight (36). This effect has been attributed to a shift in electron

density from the Fe to the Pt.

Another very interesting alloy system is that recently disclosed by Union Carbide (37) in which a supported Rh-Fe catalyst was employed to make large concentrations of $C_2$ oxygenated materials. Some of the results reported in this patent are collected in Table IX-3, and, as can be seen, addition of Fe to Rh greatly increases the production of ethanol. At much higher pressures, 2500 psig, acetic acid and acetaldehyde production both increase with the apparent methane level quite low although this last result is not firm. In most of these data, the methane level is quite high but the selective production of $C_2$ oxygenated species is quite encouraging and further catalyst and process development may increase the selectivity to control products. Metal dispersions (fraction of metal at the surface) reported for some of the catalysts used in the above work ranged from 2.7% to 22%. These values can be significantly increased with a possibly large effect on catalyst performance. The techniques for preparing supported catalysts and well dispersed alloys were discussed in Part 1. However, of particular note is the possible use of polynuclear organometallic complexes to produce well dispersed, supported alloy catalysts. It may be necessary to resort to the use of such preparative techniques to minimize the presence of the separate components that result in poor selectivity.

Other aspects of hydrocarbon synthesis where bimetallic catalysts may find application are in minimizing carbon deposition and increasing thermal stability and sulfur tolerance. The inhibition of coke formation could result by preventing the formation of

## TABLE IX-3

### SYNTHESIS OF HYDROCARBONS ON SUPPORTED RhFe CATALYSTS (a)

| Temp. (°C) | Pressure (psig) | GHSV (hr$^{-1}$) | Composition (b) %Rh | %Fe | Methane | Methanol | Acetaldehyde | Ethanol (C Efficiency, %) | Acetic Acid |
|---|---|---|---|---|---|---|---|---|---|
| 300 | 1000 | 4000 | 5.0 | --- | 37 | 0 | 24.0 | 16 | 20.0 |
| 300 | 1000 | 3900 | --- | 1.0 | 69 | 12 | 0.3 | 10 | 0.2 |
| 300 | 1000 | 2700 | 2.5 | 1.35 | 51 | 19 | 0.6 | 23 | 0.6 |
| 300 | 1000 | 3000 | 2.5 | 0.68 | 44 | 20 | 1.0 | 30 | 1.3 |
| 325 | 2500 | 11000 | 2.5 | --- | 41.0 | 1.6 | 5.2 | | 49.0 |
| 325 | 2500 | 9500 | 2.5 | 1.35 | 39.0 | 13.0 | 37.0 | | 4.0 |
| 325 | 2500 | 9300 | 2.5 | 0.135 | 5.2 | 2.3 | 13.0 | | 31.0 |
| 325 | 2500 | 8700 | 2.5 | 0.135 | 46.0 | 1.4 | 15.0 | | 36.0 |

(a)  From reference (37).

(b)  Supported on silica gel.

contiguous carbon networks on the metal surface or from an adventitious balance of hydrogenation and hydrogenolysis activity (24). Thermal stability is only of secondary importance until a highly selective catalyst is obtained. Sulfur resistance will be considered in more detail next.

An area where new catalytic materials could find extensive application is as sulfur resistant catalysts. As discussed in Section VII of Part 3 (38), combining the catalytic material with a second component with which it forms a chemical bond could inhibit the subsequent formation of a sulfide in the presence of low concentrations of $H_2S$. Since a surface sulfide layer forms even at very small ratios of $H_2S/H_2$ (39), the required heat of formation may be quite high. Formation of a simple alloy, for example NiCu where the bulk CuS phase is much less stable than NiS, may be inadequate. Bernard has shown that Cu forms a complete surface sulfide layer at 100 ppm $H_2S$ in $H_2$ and a temperature of $850^0C$ (39). At the temperatures employed in hydrocarbon synthesis, $200-300^0C$, the $H_2S$ level may be below 1ppm for monolayer sulfide formation.

Materials with a higher heat of formation that may resist the formation of a surface sulfide are borides, phosphides, and similar materials. These materials are more resistant to sulfide formation than many metals, but their activity in Fischer-Tropsch is unknown. Similarly, intermetallic compounds or Brewer compounds of the type $ZrPt_3$ and $ZrIr_3$ have high heats of formation which impart

549

high chemical and thermal stability and perhaps unusual catalytic properties. The properties and preparation of these materials have been discussed extensively in Part 2 (40), however, the catalytic properties of these compounds are unknown.

Finally, as discussed above, it should be feasible to use sulfur to control product selectivity. Sulfur addition is used industrially to modify the excessive activity of fresh naphtha reforming catalysts and also to control product selectivity (41). Recent work has shown that continuous additions of sulfur to operating Pt reforming catalysts results in improved selectivity and catalyst life (42, 43). The proposed mechanism is a partial poisoning of the Pt surface by sulfur to reduce the concentration of multiple surface sites that can result in excessive dehydrogenation and coking. The concentrations of S tested were quite high, up to 2400ppm and even at these levels good catalyst activity was maintained.

For Fischer-Tropsch synthesis, low S levels have been shown to result in an increase in liquid hydrocarbons while a larger amount shifts the product distribution back to gaseous hydrocarbons. A recent encouraging example is data obtained on supported Ni and Ru. catalysts where methane formation was the primary interest (25). At $400^{o}$C, an $H_2$/CO ratio of 4 and at atmospheric pressure, the product was between 90-100% methane. Addition of 1ppm $H_2$S to the reactant stream and subsequent saturation of the catalyst gave a steady-state product selectivity of approximately 50% methane and 50% $C_{2+}$ hydrocarbons. As the $H_2$S level was increased to 10ppm, the products shifted further toward $C_{2+}$ hydrocarbons. At lower temperatures and conditions

more representative of liquid hydrocarbon production, similar effects of sulfur are expected.

b. Bifunctional Catalysts

Since no particular type of hydrocarbon has a significantly high heat of formation per carbon atom (except methane), the problem becomes one of catalytic selectivity. One class of products that is thermodynamically preferred is isoparaffins, albeit only slightly. The large proportion of normal paraffins found in the products is a result of the synthesis mechanism on these catalytic materials. Isoparaffins and cyclic material must be generated by subsequent reaction of the straight chain hydrocarbons. The production of highly unsaturated or aromatic products represents different problems and will be discussed later.

The proportion of isoparaffins in the product stream can, in principle, be increased by including an isomerization (acidic) component in the catalyst. Thus, the catalyst may function as a bifunctional catalyst with the normal paraffins generated on the metal component, and, subsequently, isomerized on an acidic oxide support. A problem may exist in matching the reaction conditions for each of these processes. Synthesis is currently carried out at temperatures of 180 to 320$^\circ$C and in relatively small excess of hydrogen. The latter is necessary to minimize the deposition of coke on and the degradation of the acidic oxide surface. However, isomerization systems may exist in which the conditions are comparable and bifunctional systems may be practical. As an example, the Penex Process (Universal Oil Products) operates at 1500-2000 psig and 120-150$^\circ$C and isomerizes $C_4$, $C_5$ and $C_6$ (44). This particular Pt/

aluminia catalyst is formed by reacting organic chlorides with Pt/ aluminia. Conditions close to those employed in isomerization and reforming are used in the isosynthesis process where isoparaffins, especially, isobutane and isopropane are produced from $H_2$ and CO on promoted-Thoria catalysts at $450^{\circ}C$ and 4000psi. This process will be considered in more detail later. Also, the production of aromatics by the dehydrocyclization of $C_{6+}$ hydrocarbon would be of prime consideration for a bifunctional process since aromatics are high octane constituents of gasoline. Recently ERDA has announced the finding of a cooperative research effort with Mobil Oil Corporation for the further development of a single-step process for the conversion of CO and $H_2$ directly to high octane gasoline using bifunctional zeolite catalysts (45).

The problem of selectivity can be overcome by designing the reaction around products which have high thermodynamic stability or catalytic selectivity. This may significantly complicate the process and require several different catalysts and catalytic steps. A good example of this is the recent development by Mobil Oil Corporation of a process to produce high octane gasoline from CO and $H_2$ (46, 47, 48, 49, 50, 51). In this process, the $H_2$ and CO are reacted initially over a catalyst composed of a hydrogenation component and an acid dehydration component to a product composed mainly of dimethyl ether. The hydrogenation catalyst is similar to current low temperature methanol synthesis catalysts. The inclusion of an acid dehydration catalyst converts the methanol to dimethyl ether and in this manner shifts the reaction equilibrium to significantly higher conversions.

The products are then directed over a second catalyst of crystalline aluminosilicate with high silica to alumina ratio and small pore diameters to produce a liquid hydrocarbon product of high aromatic content. The important aspects of this approach are that the desired intermediate product, dimethyl ether, can be produced in large yields employing a bifunctional catalyst system of high selectivity. Although the dimethyl ether is not a desired product, it serves a useful function by being both a synthesis product that can be produced with high selectivity and also a reactant that can be selectively converted to aromatic hydrocarbons. The acid dehydration and shape selective properties of this latter catalyst must be carefully controlled to give high aromatic yield. Work on further developing of this process is continuing (45).

This process is an example of an approach that may be very useful in obtaining specific chemicals from $H_2$ and CO. Although aromatics such as benzene and toluene apparently cannot be produced from $H_2$ and CO directly due to a lack of preferential thermodynamics and catalyst selectivity, the dehydration of dimethyl ether produces aromatics with good selectivity. The unappealing intermediate, dimethyl ether, facilitates the separation of hydrogenation and dehydrogenation steps. Although more complicated than a 1-step process, such a scheme may be employed to produce other useful chemicals, and represents a novel approach to hydrocarbon synthesis.

c.  Isosynthesis

A reaction that was first developed in the early 1940's

and has received very little attention since, is the isosynthesis process. The early work has been reviewed by Cohn (52). In its original form, a catalyst consisting of thoria promoted by alumina and alkali is operated at relatively high pressures, 300 to 600 atmospheres, with a reactant composition of $2H_2$ to $1CO$. The product consists of isoparaffins, mainly isobutane, higher branched hydrocarbons and some branched olefins and aromatics. The points to be noted are that compared to Fischer-Tropsch synthesis, the conditions employed in the isosynthesis are quite unusual. The temperature is significantly higher, $450^{\circ}C$ instead of $200^{\circ}C$ and the pressure is higher, 300 atm, as opposed to 30 atm. The catalyst is also quite different in that oxides that are not reduced at the reaction conditions employed.

The production of highly isomerized hydrocarbons is in strong contrast to the normal hydrocarbons obtained in Fischer-Tropsch. However, the product distribution is centered at low molecular weights, $C_1$ to $C_4$ hydrocarbons representing over 50% of the product. The ability to produce highly branched materials and some aromatics makes the isosynthesis an important process for the production of high octane motor fuel. The product distribution must be shifted to higher carbon numbers and the activity and reaction conditions improved if the process is to become commercially viable.

The technology of the isosynthesis and the mechanism of branched hydrocarbons synthesis may be of use if it can be combined with the Fischer-Tropsch synthesis to produce more desirable branched

materials. Alternatively, the process may be optimized to selectively produce chemicals such as isobutane or olefins. Some of the better catalysts were capable of producing selectivities such as 60% isobutane while operation at high pressure favored dimethyl ether production.

### d.  Homogeneous Hydrocarbon Synthesis

Mononuclear homogeneous catalytic systems to produce hydrocarbons from CO and $H_2$ are completely unknown. This is true even for the production of methane, as discussed in Part 1, Section VI. Recently, Muetterties reported the synthesis of hydrocarbons on the homogeneous cluster complexes, $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ (53). At $140^\circ C$ and with a CO and $H_2$ pressure of 2 atm, a turnover number of $10^{-5} s^{-1}$ per cluster was observed, a rate comparable to that observed by Vannice on silica supported Ir (27). The reaction showed a high selectivity to methane. Substitution of carbonyl groups in $Ir_4(CO)_{12}$ by triphenylphosphine causes a substantial shift in the product selectivity to ethane and propane. This last result indicates an ability to control Fischer-Tropsch product selectivity with homogeneous cluster complexes.

A second example of synthesis over homogeneous catalysts is a process recently patented by Union Carbide Corporation. In one version, mononuclear rhodium complexes such as 2-pyridino-1-dicarbonyl (2,4-pentanedianato) rhodium are reacted with $H_2$ and CO ($H_2$/CO=1.5) at 20,000 psi to produce ethylene glycol and methanol (54). The pressures involved are much too high to be of industrial interest, but recent refinements of the process have led to lower pressures.

For example, the use of rhodium dicarbonyl-acetylacetonate-triiso-propanolamine, or cluster complexes such as $Rh_6(CO)_{15}^{-2}$ plus the addition of promoters such as $CsHCO_2$, $Ph_3SiH$ or $NH_4CH_3CO_2$, requires a CO and $H_2$ pressure of 8000 psi to give reasonable yields of ethylene glycol and methanol (55). If process conditions can be improved, direct glycol manufacture from CO and $H_2$ can have economic advantages (56).

Another class of homogeneous processes that utilize synthesis gas to produce hydrocarbons is homologation where methanol is reacted with CO and $H_2$ to produce higher alcohols, generally ethanol. The catalyst employed in the initial work was dicobalt octacarbonyl $CO_2(CO)_8$ and the conditions were quite stringent, 5100 psi $H_2/CO$ (1:1) and 185°C (57, 58). Ethanol represented over 50% of the product. More recent work investigated the effect of promoters such as iodine or organo phosphorous compounds (59) or iodide (60). In the latter case, the temperature was 200°C, the pressure was 4500-6000 psi and the ethanol yield was 40% at a methanol conversion of 60%.

In both the homologation chemistry and the Union Carbide process described earlier, the products are oxygenated hydrocarbons. Current understanding of the mechanisms of homogeneous catalysis support the concept that the scission of the carbon-oxygen bond cannot be accomplished by the single metal center of a mononuclear homogeneous complex (53). This is consistent with the production of ethylene glycol by the Union Carbide mononuclear rhodium catalyst where the C-O bonds remain in tact. However, the homologation adds

a $CH_2$ to the methanol in a step similar to the chemistry of Fischer-Tropsch synthesis. This includes C-O bond breaking and as such would require a multinuclear complex to be consistent with the concept outlined above. This particular approach to homogeneous $CO-H_2$ synthesis requires more investigation, especially, as it relates to the search for homogeneous catalysts for hydrocarbon synthesis.

3.  SUPPORTING RESEARCH

Basic understanding of the mechanism of catalysis and the surface properties important in controlling activity and selectivity of CO hydrogenation would be extremely useful in the development of catalysts and the search for new catalytic materials. Research in two areas should be differentiated. First, the mechanism of formation of C-C bonds on such common materials as reduced Fe and Co should be established. The mechanism described in Part 1, the polymerization of surface $H_2COH$ species and competition between polymerization and termination to control hydrocarbon chain length, is somewhat speculative and based on indirect evidence. In both methanation and Fischer-Tropsch, a partially hydrogenated surface enol of the form HCOH is formed and its reaction to methane or condensation to form C-C hydrocarbon bonds is assumed to be the slow step. Recent data, however, indicate that the slow step may be scission of the C-O bond of the adsorbed CO. A number of recent experimental results support this particular mechanism. The measurement of the kinetic isotope effect showed that on supported Ni, Ru and Pt, the ratio of rates

for the reaction of $H_2$ + CO and $D_2$ + CO proceed at identical rates implying that hydrogen is not involved in the rate determining step (61). Studies on Ni and Ni-Cu alloys show that an ensemble of contiguous surface sites are required to dissociate C-O prior to reaction with hydrogen (62). Also, recent LEED and UPS measurements on Ni show that co-adsorption of $H_2$ and CO does not lead to formation of a surface enol complex and decomposition of the CO may be required before hydrogenation of the CO can proceed (63). These data are consistent with in situ infrared spectroscopic examination of alumina supported Ru, Rh and Pt catalysts that show the surface is covered predominately by adsorbed CO during reaction of $H_2$ and CO to form $CH_4$ and no evidence of a surface formyl complex was obtained (64). Important surface properties such as strength of CO binding, simultaneous adsorption of CO and $H_2$ and the need of other structural or electronic properties should be clarified. This should aid in understanding the selectivity variation observed between metals and the action of promoters such as potassium.

The second line of basic research, not unconnected with that described above, is the comparative study of $H_2$ + CO catalysis on a variety of materials that show widely different selectivity in the reaction of $H_2$ and CO. Some materials, such as ZnO and Cu, selectively produce methanol. Iron and Co produce alcohols, olefins and paraffins under certain conditions and almost totally paraffins under other conditions. Still other metals, Ni, Pt, etc., produce mostly methane. Such variation is generally ascribed to relative hydrogenation activity

of the catalytic material, but the controlling factors in such gross selectivity changes is not well understood. With such widely varying surfaces and metal oxidation states, the adsorbed species or reaction intermediates may well be different. Certainly the stability and binding strength of a surface species would be quite different on such a variety of materials.

D. CONCLUSIONS

The product distribution in hydrocarbon synthesis from CO and $H_2$ is kinetically controlled in nearly all cases. The greater stability of methane leads to significant yields for a variety of conditions and catalysts, a major problem when liquid hydrocarbons are wanted. The difficulty in obtaining a kinetic selectivity arises from the mechanism of hydrocarbon synthesis, a polymerization process. However, past catalyst performance teaches that the position of the product distribution can be shifted and narrowed somewhat by changes in operating conditions or catalyst composition. The desire for even more specific processes makes further development of synthesis catalysts imperative. Similarly, the development of sulfur resistant catalysts capable of operating in low levels of sulfur, 10 to 1000ppm, would greatly improve the efficiency of the hydrocarbon synthesis process.

The effect of promoters, the importance of the support and the variation in catalyst activity and selectivity with changes in preparation procedure make this a good area for short-term development work. The preparation of highly dispersed-supported catalysts and

multicomponent materials by the preparative techniques described in Part 1 will permit an extensive evaluation of support and promoter effects. However, it cannot be overemphasized that the conditions at which the test is run are very important and can greatly affect the activity and product distribution. Not only should conditions close to those used in current processing schemes be used, but a variety of conditions including temperature, pressure, and $H_2/CO$ ratio should be evaluated with detailed product analysis to monitor product composition and changes in catalyst selectivity.

Alloys, complex oxides and new catalytic materials should be explored because of the almost complete lack of data for these materials for hydrocarbon synthesis. They should also be tested for sulfur resistance. Some of the well characterized alloy systems such as NiCu, CuRu, PdAu, etc., and materials such as cluster oxides, e.g., $Mg_2MoO_8$ containing $Mo_3$ clusters, represent short-term efforts since these materials are known and their catalytic properties have been studied albeit for other reactions. The development of optimum alloy systems, the clarification of important catalytic properties such as oxidation state, electronic and structural properties, etc., will be of a long-term nature and will be greatly aided by an indepth understanding of the mechanism of higher hydrocarbon synthesis. This latter area, together with a better understanding of the important surface properties controlling the course of the synthesis reaction represents an important basic research area where effort is needed.

Finally, bifunctional catalysts and multi-step processes have recently been shown to be extremely promising areas. New chemistry such as that uncovered for the bifunctional systems discovered by Mobil should be researched and developed in detail. Such multi-step processing of $CO-H_2$ mixtures may permit the selective production of a wide variety of hydrocarbon materials.

# E. REFERENCES

1.  Anderson, R. B., in _Catalysis_ (P. H. Emmett, Ed.), Vol. IV, p. 1.
    Reinhold, New York, 1956.

2.  Storch, H. H., Golumbic, N., and Anderson, R. B., _The Fischer-Tropsch
    and Related Syntheses_. John Wiley and Sons, Inc., New York, 1951.

3.  Anderson, R. B., in _Catalysis_ (P. H. Emmett, Ed.), Vol. IV, p. 109.
    Reinhold, New York, 1956.

4.  Friedel, R. A., and Anderson, R. B., J. Amer. Chem. Soc. _72_, 1212
    (1950), and J. Amer. Chem. Soc. _72_, 2307 (1950).

5.  Anderson, R. B., in _Catalysis_ (P. H. Emmett, Ed.), Vol. IV, p. 213ff.
    Reinhold, New York, 1956.

6.  Weitkamp, A. W., Seelig, H. S., Bowman, N. J., and Cady, W. E.,
    Ind. Eng. Chem. _45_, 343 (1953).

7a. Pichler, H., and Schulz, H., Chem. Eng. Tech. _42_, 1162 (1970).

7b. Nefedov, B. K., and Eidus, Ya T., Russian Chemical Reviews _34_,
    272 (1965).

8.  Bienstock, D., Jimeson, R. M., Field, J. H., and Benson, H. E.,
    U. S. Bureau of Mines R. I. 5655 (1960); Field, J. H., Bienstock, D.,
    Forney, A. J., and Demski; R. J., U. S. Bureau of Mines R. I. 5871
    (1961).

9.  Karn, F. S., Shultz, J. F., Kelly, R. E., and Anderson, R. B., Ind.
    Eng. Chem. Prod. Res. Dev. _2_, 43 (1963).

10. Karn, F. S., Shultz, J. F., Kelly, R. E., and Anderson, R. B., Ind.
    Eng. Chem. Prod. Res. Dev. _3_, 33 (1964).

11. Part 3, Section VII, p. 460.

12. Herington, E. F. G., and Woodward, L. A., Trans. Faraday Soc. _35_,
    958 (1939).

13. Anderson, R. B., in _Catalysis_ (P. H. Emmett, Ed.), Vol. IV, p. 246.
    Reinhold, New York, 1956.

14. Craxford, S. R., Trans. Faraday Soc. _42_, 576 (1946).

15. Part 3, Section VII, p. 466.

16. White, G. A., Roszkowski, T. R., and Stanbridge, D. W., Amer. Chem. Soc., Div. Fuel Chem., Prepr. 19 (3), 57 (1974); Methanation of Synthesis Gas (L. Seglin, Ed.), Advances in Chemistry, Vol. 148, p. 138. Amer. Chem. Soc., Washington, 1975.

17. Greyson, M., in Catalysis (P. H. Emmett, Ed.), Vol. IV, p. 473. Reinhold, New York, 1956.

18. Field, J. H., Bienstock, D., Forney, A. J., and Demski, R. J., U. S. Bureau of Mines R. I. 5871 (1961).

19. Hoogendoorn, J. C., presented at Clean Fuels and Coal Symposium, 1973.

20. Chem. Eng. News, p. 24, July 19, 1976.

21. Part 3, Section II.

22. Vannice, M. A., and Garten, R. L., U. S. Patent No. 3,941,819, March 2, 1976.

23. Vannice, M. A., J. Catal. 37, 449 (1975).

24. Sinfelt, J. H., Carter, J. L., and Yates, D. J. C., J. Catal. 24, 283 (1972); Sinfelt, J. H., Barnett, A. E., and Carter, J. L., U. S. Patent No. 3,617,518 (1971).

25. Dalla Betta, R. A., Piken, A. G., and Shelef, M., J. Catal. 40, 173 (1975).

26. Part 1, Section VI, p. 93.

27. Vannice, M. A., J. Catal. 37, 462 (1975).

28. Boudart, M., Cusumano, J. A., and Levy, R. B., New Catalytic Materials for the Liquefaction of Coal, Report RP-415-1, Electric Power Research Institute, October 30, 1975.

29. Dalla Betta, R. A., and Boudart, M., in Catalysis (J. Hightower, Ed.), p. 1329. North Holland Publishing Co., Amsterdam/London, 1972; Gallezot, T., Alarcon-Diaz, A., Dalmon, J. A., Renouprez, J. R., and Imelik, B., J. Catal. 39, 334 (1975).

30. Gallezot, P., Datka, J., Massardier, J., Primet, M., and Imelik, B., Sixth International Congress on Catalysis, London, July 12-16, 1976, to be published.

31. Chukin, G. D., Landau, M. V., Kruglikov, V. Ya., Agievskii, D. A., Smirnov, B. V., Belozerov, A. L., Asrieva, V. D., Goncharova, N. V., Radchenko, E. D., Konovalchikov, O. D., and Agafonov, A. V., Sixth International Congress on Catalysis, London, July 12-16, 1976, to be published.

32. Part 1, Section II, p. 4ff.

33. Rabo, J. A., Schomaker, V., and Pickert, P. E., Proc. Int. Congress Catalysis, 3rd., 1964, North Holland Pub. Company, Vol. 2, p. 1264, (1965).

34. Part 1, Section VII, p. 113ff.

35. Bartholomew, C. H., ERDA Project No. E(49-18)-1790, Annual Technical Progress Report, May 6, 1976.

36. Vannice, M. A., and Garten, R. L., J. Molec. Catal. 1, 201 (1976).

37. Bhasin, M. M., German Patent No. 2,503,233, July 31, 1975.

38. Part 3, Section VII, p. 474.

39. Benard, J., Catal. Rev. 3 (1), 93 (1969).

40. Part 2, Section III, p. 246.

41. Maxted, E. B., Adv. in Catal. Relat. Sub. 3, 129 (1951).

42. Hayes, J. C., Mitsche, R. T., Pollitzer, E. L., and Homeier, E. H., Amer. Chem. Soc., Div. Petrol. Chem., Prepr. 19 (2), 334 (1974).

43. Haensel, V., Donaldson, G. R., Riedl, F. J., Proc. Third International Congress on Catalysis, Amsterdam, 298 (1964).

44. Thomas, C. L., Catalytic Processes and Proven Catalysts, p. 17. Academic Press, New York, 1970.

45. Heinemann, H., private communication.

46. Chang, C. D., and Silvestri, A. J., U. S. Patent No. 3,894,102 (July 8, 1975).

47. Chang, C. D., Silvestri, A. J., and Smith, R. L., U. S. Patent No. 3,894,103 (July 8, 1975).

48. Chang, C. D., Lang, W. H., and Silvestri, A. J., U. S. Patent No. 3,894,104 (July 8, 1975).

49. Chang, C. D., Silvestri, A. J., and Smith, R. L., U. S. Patent No. 3,894,105 (July 8, 1975).

50. Chang, C. D., Lang, W. H., and Silvestri, A. J., U. S. Patent No. 3,894,106 (July 8, 1975).

51. Butler, S. A., Jurewicz, and Kaeding, W. W., U. S. Patent No. 3,894,107 (July 8, 1975).

52.  Cohn, E. M., in Catalysis (P. H. Emmett, Ed.), Vol. IV, p. 443. Reinhold, New York, 1976.

53.  Thomas, M. G., Beier, B. F., and Muetterties, E. L., J. Amer. Chem. Soc. 98, 1296 (1976).

54.  Walker, W. E., and Cropley, J. B., German Patent No. 2,426,495 (June 19, 1973); CA 82:139312Q; Pruett, R. L., and Walker, W. E., U. S. Patent No. 3,833,634 (September 3, 1974).

55.  Kaplan, L., U. S. Patent No. 3,944,588 (January 2, 1976); CA 84:164152M.

56.  Brownstein, A. M., Chem. Eng. Prog. 71, 72 (1975).

57.  Wender, I., Friedel, R. A., and Orchin, M., J. Amer. Chem. Soc. 71, 4160 (1949).

58.  Wender, I., Friedel, R. A., and Orchin, M., Science 113, 206 (1951).

59.  U. S. Patent No. 3,248,432 (April 26, 1966).

60.  Mizoraki, T., and Nakayama, Bull. Chem. Soc. Japan 37, 236 (1964).

61.  Dalla Betta, R. A., and Shelef, M., to be published.

62.  Araki, M., and Ponec, V., submitted for publication in Journal of Catalysis.

63.  Conrad, H., Ertl, G., Küppers, J., and Latta, E. E., Sixth International Congress on Catalysis, London, July 12-16, 1976, to be published.

64.  Dalla Betta, R. A., and Shelef, M., to be published.