# ACKNOWLEDGMENT

# ABSTRACT

One of the important factors for the commercial success of the conversion of coal to synthetic fuels is the development and improvement of a number of catalytic processes and reactions. This study reviews key advances in catalysis and related fields which are expected to be important for R & D programs in the synthetic fuels industry. The advances include developments in multimetallic catalysis and other novel catalytic materials; the understanding of the effects of catalyst-support interactions, surface morphology and crystallite size; the development of catalyst characterization techniques, novel catalyst preparation procedures, studies on poisoning and regeneration, and the present understanding of the mechanism of reactions important for the conversion of coal to synthetic fuels. Also discussed are the relevant aspects of supporting disciplines such as reactor engineering, inorganic chemistry and materials science. The role played by these advances in the improvement of a number of specific coal conversion and upgrading processes is critically assessed.

PART 1

## SURVEY OF ADVANCES IN CATALYSIS

### I. INTRODUCTION

The conversion of coal to synthetic fuels encompasses a number of catalytic processes and reactions, the most important of which are summarized in Table I-1. In addition to the various routes currently being explored to produce gaseous and liquid fuels from coal, this table includes many of the reactions which have been developed over the last 20 years to refine petroleum. Similar technology is expected to be applicable for upgrading coal liquids. The catalytic aspects of the coal conversion industry therefore includes the potential utilization of a significant fraction of presently known catalytic materials, including metals, oxides, solid acids, and sulfides.

Paralleling this projected extensive development of catalyst technology for the conversion of coal are a number of technical challenges which are familiar to the catalytic scientist and engineer. These include control of selectivity and activity, minimizing activity decline by poisoning, sintering and mechanical degradation, the development of cost-effective catalyst regeneration procedures, and optimization of reactor design variables which minimize heat and mass transfer limitations. It is well known that, because of the complex nature of coal, these challenges are more significant than those encountered in the development of petroleum processes.
However, it is expected that the advances in the field of catalysis which have taken place over the last decade will play a significant role in solving many of the technical constraints imposed on coal conversion processes.

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## TABLE I-1

## CATALYTIC REACTIONS IN COAL CONVERSION

| Process | General Reactions | Specific Reactions/Products |
|---|---|---|
| Direct Liquefaction | Hydrogenation Cracking Hydrofining | Aromatic Liquids HDS, HDN |
| $CO/H_2$ Synthesis | Fischer-Tropsch | Methane Hydrocarbon Liquids Alcohols Chemicals |
| Water Gas Shift | | Hydrogen |
| Direct Gasification | Hydrogasification Oxidative Gasification | Methane Synthesis Gas |
| Liquids Refining and Upgrading | Cracking Reforming Hydroforming | Hydrogenation Dehydrogenation Dehydrocyclization Isomerization Hydrogenolysis HDS, HDN |

The present study was undertaken in order to provide a perspective of the role which key developments in catalysis and related fields will play in the solution of the problems of catalytic coal conversion. In order to provide the background information for such an analysis, the first part of the study highlights the most significant advances that have been reported over the last decade in catalysis and related disciplines. Advances in catalysis are discussed in Part 1, while those in supporting disciplines such as solid state chemistry, materials science, reactor engineering, surface science, and organometallic chemistry are treated in Part 2. Included in these discussions are areas that are considered relevant and important to the solution of the catalytic problems of coal conversion, but in which there has been only limited activity over the last ten years. The need for further research in these areas is stressed, in particular when applicable to the specific coal processes considered in Part 3.

The review and discussion of key advances in catalysis, which is the topic of the present report, has been sub-divided into six broad areas: multimetallic catalysis; effects of catalyst-support interactions, particle size, and surface morphology on the behavior and properties of catalysts; catalyst characterization; catalyst preparation; effects of poisoning and regeneration; and a discussion of mechanisms of importance to catalytic coal conversion. While the emphasis in these areas is on work conducted during the last decade, some relevant information concerning earlier work is also included. In addition to a review of the main research topics, the general implications of these topics to coal conversion are outlined. These implications will be discussed in more detail in Part 3 of this study, where specific coal conversion processes are considered.

## II. MULTIMETALLIC CATALYSTS

### A. INTRODUCTION

One of the significant advances in catalysis over the last decade is the development of multimetallic systems for the control of catalytic properties. The impact of this research on technology is already apparent, and is likely to increase substantially over the next decade. For example, new multimetallic catalysts with high activity and unprecedented activity maintenance have been commercialized for the catalytic reforming of petroleum naphthas to high octane gasoline (1-4). Similar systems are finding utility in other petroleum processes such as isomerization (5), hydrocracking (6), and hydrogenation (7). In the petrochemicals field, research on bimetallic catalysts has led to improved Pd-Au catalysts for the synthesis of vinyl acetate (8), and to more selective catalysts (e.g. Ag-Au, Cu-Au) for the partial oxidation of olefins (9, 10). Still other studies have uncovered supported alloys such as Pt-Co (11) which have increased thermal stability and resistance to sintering. Product selectivity is a critical parameter which can now be optimized for many processes by the use of multimetallic systems. For example, for hydrocarbon reactions such as dehydrocyclization (12) and aromatic hydrogenation (13), it is possible to minimize cracking reactions (hydrogenolysis) while maintaining very high hydrogenation activity. This can give a significant economic advantage by maximizing the yield of valuable liquid products.

It is clear that multimetallic catalysts will play a major role in present and emerging petroleum and petrochemical technologies. Therefore,

it was considered imperative to reveiw the advances which have been made in this area, and to highlight those aspects which are likely to impact on the catalytic conversion of coal.

Although some patents and publications disclose multimetallic catalysts containing three or more metals, the greatest understanding exists for bimetallic systems. For this reason, the present discussion will be limited primarily to the latter. However, many of the basic principles discussed are applicable to more complex systems. This section is divided into three parts. First, the general nature of bimetallic catalysts is described, emphasizing highly dispersed systems. Mention is made of catalyst preparation and characterization where applicable. Next, the catalytic properties of bimetallic systems are discussed, with emphasis on those aspects which may have applications for reactions involved in the catalytic conversion of coal. Finally, specific applications of multimetallic catalysts to the latter are briefly reviewed as a prelude to Phase II of this study where these applications are treated in detail for specific processes.

## B. GENERAL NATURE OF BIMETALLIC CATALYSTS

Bimetallic systems have been of interest to catalytic scientists for some time. Much of the initial work in this area was carried out to investigate the relationship between catalytic activity and the electronic structure of metals, and dates back to the early concepts proposed by Dowden (14, 15) and Schwab (16). The approach in this work consisted of investigating catalytic activity as a function of alloy composition, the latter determining the electronic properties of the metal. Alloys of a Group VIII and a Group IB metal (e.g. Ni-Cu) have received particular attention in this regard because it has been commonly suggested that the d electrons of the metal play an important role in determining catalytic activity. For these alloys the IB metal is considered to donate s electrons to the d band of the Group VIII metal and thus, by this model, it is possible to control the d-electron density. Bimetallic alloys of Group IB with Group VIII metals have been studied by a number of workers for such reactions as the hydrogenation of benzene (17-20) and ethylene (21, 22). Some of these early concepts, while useful as working hypotheses, are now known to be inadequate for understanding the properties of bimetallic systems. More realistic models such as the virtual bound state concept have been developed (23, 24). These models provide a better rationale than the simple band picture for many of the physical, chemical, and catalytic properties of bimetallic systems.

The development of new characterization techniques has also played a significant role in understanding the properties of bimetallic catalysts (25). For example, by the use of surface analysis techniques such as Auger spectroscopy and selective adsorption, it has been found

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that the surface and bulk compositions of a bimetallic catalyst can differ significantly (13, 20). Such information is critical for the interpretation of catalytic data for bimetallic systems (26).

In general, bimetallic catalysts can be divided into two broad classes, supported and unsupported. The latter has received extensive attention over the years because single crystals, films, and powders of alloys are, in general, easier to study and characterize. More recent efforts, however, have been directed toward supported bimetallic catalysts because of the technological importance of these systems.

Supported bimetallic catalysts can be further subdivided into two types, alloys and clusters. An alloy catalyst consists of two mutually soluble metals with a composition which is well defined by a bulk phase diagram. The bulk composition of a bimetallic alloy catalyst is usually obtainable by x-ray diffraction methods. In many cases there is an almost linear relationship between lattice constant and alloy composition (Vergard's Law). These measurements can be readily made if the catalyst exists in a sufficiently large crystallite size ($> 30\overset{o}{A}$) to minimize line broadening effects in the x-ray pattern. Highly dispersed bimetallic alloy catalysts can approach crystallite sizes for which most of the metal atoms are surface atoms. These cannot be easily studied by x-ray diffraction and are called bimetallic clusters (26). This terminology is preferred to the term alloy because many systems of interest in this category include metallic combinations which do not correspond to known bulk alloys (26). The existence of such bimetallic clusters for systems with major miscibility limitations in the bulk implies that the degree of metal dispersion has a strong effect on the stability of bimetallic clusters. Consequently, physical or

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chemical conditions which favor crystallite growth for such systems can cause phase separation of the two constituent metals.

Bimetallic cluster catalysts are usually supported on a high surface area material because it is difficult to maintain highly dispersed metals in the unsupported state without resultant sintering and crystallite growth. This is particularly a problem during use where high temperatures may occur. As mentioned above, such crystallite growth can cause phase separation for some cluster catalysts. Another reason for supporting these catalysts is to maximize catalyst utilization. This is of primary concern when noble metals are involved and maximum activity per gram of metal is necessary for economic reasons. A detailed description of the preparation of bimetallic catalysts is given elsewhere (25, 27).

## C. PHYSICAL PROPERTIES OF BIMETALLIC CATALYSTS

Various techniques have been employed for the characterization of bimetallic catalysts. These include gas adsorption (28), x-ray diffraction (29), magnetic measurements (30), Auger spectroscopy (31), photoelectron spectroscopy (32), and extended x-ray absorption fine structure analysis, EXAFS (33). It is not necessary to review these techniques here since they have recently been treated in some detail with respect to catalyst characterization (25). Most of these techniques give an indirect measurement of at least one of three properties of bimetallic catalysts: surface area and composition, crystallite size, and the chemical state of the surface metal atoms. These parameters are briefly discussed in the following two sections concerning thermal and chemical stability. Emphasis is given to supported catalysts.

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## 1. THERMAL STABILITY

The effects of temperature on a bimetallic catalyst depends on a number of factors including initial metal dispersion, nature of the support, and the gaseous environment. Much has been learned over the past decade concerning catalyst sintering (34, 35) and metal support interactions (36, 37). Some discussion concerning these areas is given in Part 2, however it is useful to briefly mention those aspects which are pertinent to bimetallic systems.

Crystallite growth of highly dispersed bimetallic catalysts can cause two phenomena to occur. The first is phase separation of the two metals with increasing crystallite size. This is predominantly a potential problem with bimetallic clusters composed of two immiscible metals. For example, ruthenium and copper do not form bulk alloys, yet these metals do form relatively stable bimetallic clusters (26). If the bimetallic RuCu cluster is sintered at high temperatures, the two metals can separate. However, in the dispersed state there is a significant interaction between the two metals which, as discussed below, markedly modifies catalytic properties. This same interaction also gives rise to an increased thermal stability. This is indicated by the decreased tendency for copper to sinter in the RuCu cluster relative to a supported copper catalyst (26). Similar effects have been observed for OsCu (26) and PtCo (11). Bimetallic systems therefore offer a means to synthesize catalysts of higher thermal stability.

The second effect observed as a result of crystallite growth is predictable from the thermodynamic models for dispersed bimetallic systems (38-40), namely a change in surface composition with crystallite size. This effect is observed even for "miscible" systems such as

Ni-Cu (41, 42) and Ni-Au (43), and is therefore not restricted to immiscible combinations like Ru-Cu or Os-Cu. The change in surface composition of bimetallic crystallites simply reflects the thermodynamic driving force for the metal with the lowest surface energy to concentrate at the surface. This enrichment increases with decreasing crystallite size (38-40). Of course, in the limiting case of completely dispersed bimetallic clusters, this concept does not apply. However, it does apply even to the smallest of crystallites, e.g. $12\overset{o}{A}$, for which surface segregation or enrichment can occur (38) and may have marked effects on catalysis. More recent work has shown that the chemisorption of gases can alter surface composition, and therefore studies are now being directed at measurements of surface composition at the conditions of catalysis (44-45).

Thermal stabilization, phase separation, and surface composition changes are phenomena which have been recognized as significant and quantified only over the last several years.

## 2. CHEMICAL STABILITY

An important criterion which a catalyst must meet in a number of reactions involved in the catalytic conversion of coal is that of chemical stability with respect to the environment in which it must function. By far the two major demands on a catalyst in such a typical environment are compatibility with sulfur and stability with respect to oxidative regeneration (25). Each of these facets is discussed in some detail in Section VI , however some general comments are pertinent for bimetallic catalysts.

With respect to sulfur, it has recently been shown (25) that all metals can sulfide in an environment such as that encountered in

the direct liquefaction of coal to boiler fuels where $H_2S$ levels of one percent and higher are common. Alloying or formation of bimetallic clusters is not expected to have a significant effect on the thermodynamic driving force for sulfidation under these conditions (25). However, at lower levels of sulfur contamination (e.g. 10-1000 ppm), cluster or alloy formation may alter the poisoning effects although there are only few data in the literature to support this contention (46). The example of the resistance of the very stable intermetallic compound, $ZrPt_3$, to sulfidation has previously been discussed (25), and it was shown that the more exothermic the heat of formation of the alloy, the greater is its thermodynamic resistance to sulfidation. Similar arguments hold for dispersed systems where bimetallic interactions may affect the nature of the metal-sulfur interaction. The effects of increased metal dispersion are expected to enhance metal-sulfur interactions unless a metal-support effect is present. The latter is expected to be most important at high dispersions, and could cause increased sulfur resistance (See Sections III and IV).

The problems encountered for bimetallic catalysts in oxidative regeneration are two-fold. The first is a common concern for the regeneration of all supported metal catalysts, namely sintering of the metal phase. This occurs even when carbon burn-off is controlled carefully by using low oxygen concentrations. The problems of local hot-spotting and high surface temperatures are commonly encountered (47-48). After several regeneration cycles (see general discussion of regeneration in Section VI), the crystallites grow to a size which corresponds to a decrease in active metal surface area, and therefore, to lower activity. However, for bimetallic catalysts an additional factor

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is important. This involves changes in surface composition and phase segregation or separation with increased crystallite size. These effects have been discussed above. For some bimetallic systems (e.g. Pt-Co, Pt-Pd, Ru-Cu) there is actually an increased thermal stability with respect to sintering (11, 26). There is also the possibility that a high temperature oxidative environment can generate a mixed oxide system for some bimetallic catalysts (especially for non-noble metal systems). Cycling between the metallic and oxide state in some instances has been reported to give rise to the formation of supported bimetallic catalysts with a different distribution of surface compositions than the original catalyst (49). These effects are presently being studied (49).

From the results of studies of bimetallic catalysts, it appears that these materials may offer a possibility for diminishing the effects of sulfur as long as these catalysts are not used at very high sulfur activity levels ($<$ 1 percent). They also offer a means of improving thermal stability, however the preparative variables must be well understood to do this. This is an area of increasing research interest.


D. CATALYTIC PROPERTIES

Numerous studies have been reported concerning the catalytic properties of bimetallic systems (13, 25-27, 50). However, only over the last several years has there been a significant effort to relate catalytic data to surface properties. This is primarily because variations in alloy surface composition from that of the bulk were not considered in earlier studies. Also, only recently have studies dealt

with highly dispersed supported bimetallic systems (26, 49).  From these studies it is clear that catalyst preparation variables can have a marked effect on the nature of the bimetallic catalyst (25, 27).

In the following three sections, the catalytic properties of bimetallic catalysts are discussed in terms of effects concerning catalytic activity, activity maintenance, and selectivity.

## 1. ACTIVITY

Although bimetallic systems can be used to affect catalytic activity, it is more informative to consider selectivity data.  This is because often several reactions can occur for a given process, and it is usually necessary to maximize the yield of only one of the resulting products.  For example, in catalytic reforming or hydrocracking, branched paraffins and aromatics are preferred products, and it is necessary to minimize the yield of light gases such as $CH_4$ and $C_2H_6$. As will be discussed later, bimetallic catalysts offer a means of increasing the selectivity to the valuable liquid products for such a process.

In terms of activity there have been a number of studies of both simple test reactions and industrial processes.  In these studies, bimetallic catalysts have been reported to have increased catalytic activity. For example, the combination of Group IB with Group VIII metals is reported to increase hydrogenation activity.  Thus, Ni-Cu (13) and Ru-Cu (26) show higher rates for cyclohexane dehydrogenation than do the pure metals.  However, it has been remarked by some investigators that this may not be due to greater intrinsic activity of the bimetallic catalyst, but to less carbon fouling of the bimetallic surface as compared to that of the pure metals (50).  It is likely, for certain systems which involve metals with very high hydrogenolysis activity,

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that both factors may be involved. Similar promotional effects have been seen for olefin hydrogenation reactions using Pd-Au (7) and Ni-Cu (51-52).

Recently, bimetallic catalysts have been discovered which show marked activity increases for the reactions involved in the catalytic reforming of petroleum naphthas to high octane gasoline. This has brought about the commercialization of a series of these catalysts, including Pt-Re (3), Pt-Pb (53), $Pt_3Cu$ (54), and a multi-metallic system called KX-130 (1). This increase in activity is clearly shown in a study that compares Pt-Re and KX-130[a] with a conventional platinum reforming catalyst (1). This study involved the conversion of a Middle East paraffinic naphtha at 150 psig and 930°F to high octane gasoline (102.5 RON). It was found that the initial activity for Pt-Re is comparable to Pt, but the former catalyst has a marked increase in activity maintenance (See Section II.D.2). The initial activity for the KX-130 catalyst is at least four times higher than the traditional platinum catalysts. The activity for these catalysts was measured by the space velocity required to give a constant octane of 102.5[b]. The liquid yields for all three catalysts were comparable. From this work and that described above, it is clear that bimetallic systems can be used to improve the activity of catalytic reactions.

2. ACTIVITY MAINTENANCE

In commercial operation a catalyst can undergo poisoning or fouling (See Section VI). For hydrocarbon reactions, this is usually

a. The composition of this multimetallic system has not been disclosed in the open literature.

b. Octane number is directly related to the aromatic content in the gasoline product.

due to poisoning of metal sites by substances like sulfur or to coke accumulation with time on stream. Bimetallic systems have demonstrated applications in overcoming these problems for some reactions. As mentioned previously, this might involve increased resistance to sulfur poisoning. For carbon fouling it could be due to decreased coke yields or increased coke tolerance. These improvements enhance product yields and catalyst life, and therefore can have significant effects on process economics.

An example of the effect of alloying on activity maintenance is provided by the Pt-Re and KX-130 catalysts mentioned in the previous section. These catalysts show significant resistance to coke deactivation. This appears to be due to the deposition of substantially lower amounts of coke (1-3, 50) than that observed for conventional platinum catalysts (1). After 300 hours on stream, the conventional platinum catalyst decreased by 73 percent from its initial activity, Pt-Re decreased by 24 percent and KX-130 showed no measurable decrease in activity. This increased activity maintenance may occur for two possible reasons. First, the self-poisoning effects caused by coke accumulation come about from polymerization of "acetylenic" residues. The formation of these residues is thought to require at least three contiguous metal sites (50). Contiguous sites can be disrupted by alloying an active metal with an inert metal (e.g. Pt-Au, Pt-Sn, or Pt-Cu). Therefore, alloy formation can dilute the primary active centers and inhibit coke generation. A second possibility is a high but proper balance of hydrogenation and hydrogenolysis activity. The latter promotes cracking of surface residues, and the former guarantees facile hydrogenation of the cracked species, and therefore inhibits

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polymerization of carbon species to coke. Both of these models require a bimetallic catalyst with a proper balance for these key functions.

The balance of hydrogenation to hydrogenolysis activity can be controlled for a catalyst by the appropriate combination of metals and catalyst preparation (See Section II.D.3). As an example, a general finding which has been uncovered (25-27, 55) shows that addition of Group IB metals (Cu, Ag, or Au) to metals of Group VIII which have high hydrogenolysis/hydrogenation ratios (e.g. Ru, Rh, Ir, Ni) can be used to continuously adjust this ratio. As discussed in the next section, this occurs because the IB metal selectively inhibits hydrogenolysis activity but maintains or promotes hydrogenation activity. This can have a significant effect on the equilibrium levels of coke deposited on the catalyst as well as product selectivity.

### 3. SELECTIVITY

It is clear from the discussion in the previous two sections that catalyst activity and activity maintenance are very much related for bimetallic catalysts. The final parameter of interest, and one which is also inter-related with activity and activity maintenance, is catalyst selectivity. Selectivity is a ratio of activities or rate constants, and is a measure of the yield to a given product. Only over the last several years have catalytic studies involving bimetallic systems been directly concerned with selectivity. The majority of prior studies were involved almost solely with catalytic activity (13, 25-27).

Perhaps the most widely studied bimetallic system is that of Ni-Cu alloys. In studying this system, Sachtler and co-workers found a marked enhancement in the selectivity of Ni by alloying with Cu for

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reactions involving only scission of carbon-hydrogen bonds (56). This was due to the suppression of carbon-carbon bond hydrogenolysis. Similar effects were observed by Sinfelt and co-workers for ethane hydrogenolysis and cyclohexane dehydrogenation (13). In the later study the hydrogenolysis of ethane to methane and the dehydrogenation of cyclohexane to benzene were investigated over a series of Ni-Cu alloys. These alloys were characterized by adsorption, x-ray diffraction, and magnetic measurements. The addition of copper to nickel was found to have markedly different effects for the two reactions. For ethane hydrogenolysis, the catalytic activity decreased by several orders of magnitude with increasing copper concentration. With cyclohexane dehydrogenation, however, catalytic activity increased initially with the first small amounts of copper, and then remained insensitive to alloy composition over a wide range, finally decreasing sharply at very high Cu/Ni atom ratios. These data can be rationalized on the basis of the rate limiting steps for the two reactions. For ethane hydrogenolysis, an increased concentration of Ni-Cu pairs on the surface decreases the number of diadsorbed ethane intermediates since hydrocarbons adsorb only weakly on copper. If carbon-carbon bond scission is the rate limiting step for this reaction, the decrease in reactivity of nickel with the addition of copper can be understood. For cyclohexane dehydrogenation, the rate-limiting step is assumed to be desorption of benzene. In this case, copper is thought to decrease the binding energy of benzene and, therefore, the rate increases. The relative insensitivity of dehydrogenation reaction rate over Ni-Cu alloys of comparable concentration is attributed to the relatively constant surface composition in this range as determined by $H_2$ chemisorption.

A similar interpretation of these data is given by Burton and Hyman using a model for segregation of alloy surfaces (57).

Selectivity effects have also been observed for supported bimetallic cluster catalysts although data for these catalysts are few (26, 49). In one case (26), silica-supported Ru-Cu and Os-Cu catalysts were studied for ethane hydrogenolysis and cyclohexane dehydrogenation in a manner similar to that described for the unsupported Ni-Cu alloys (13). The results are also similar in that in the highly dispersed state, copper interacts strongly with ruthenium and osmium, and decreases the hydrogenolysis activity of these metals, even though copper is virtually immiscible with these metals in the bulk.

More recent work (58) with unsupported Ru-Cu catalysts has shown the same effects in spite of the miscibility problem at larger crystallite sizes. There is definite evidence of interaction between the two metals. The presence of copper decreases the capacity of ruthenium for hydrogen chemisorption, and also suppresses markedly the catalytic activity for hydrogenolysis of ethane to methane. The ethane hydorgenolysis activity of a Ru-Cu catalyst is strikingly related to its capacity for strong hydrogen chemisorption. The interaction between copper and ruthenium for these unsupported bimetallic systems occurs at the surface, and is similar to that which would exist if copper were to "chemisorb" on ruthenium. The state of dispersion for Ru-Cu catalysts has a major influence on the effect of the copper. The atomic ratio of copper to ruthenium required for a given degree of coverage of the surface by copper increases with increasing dispersion, as is clearly reflected by the results for hydrogen chemisorption and ethane hydrogenolysis. It is clear from these examples that the

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inhibition of the hydrogenolysis activity for the Group VIII metals by alloying with Group IB is well established.

Selectivity effects using bimetallic catalysts have been observed for a number of other hydrocarbon reactions. For example, both cyclization and skeletal isomerization of paraffins are enhanced by alloying a "catalytic" metal such as platinum with an inert metal such as gold or copper (59). Examples of this effect have been described by Ponec and Sachtler for n-hexane isomerization (60) over Ni-Cu alloys and by Ponec and co-workers (59) for hexane cyclization over Pt-Au alloys. The reason for this enhancement in selectivity is also ascribed to an increase in the number of isolated metal atoms, e.g. Pt in an Au matrix. This leads to an enhancement in selectivity to products which require single sites and a decrease in those products arising from pathways requiring several contiguous active metal sites. A further feature of dilute active sites relevant to activity maintenance for hydrocarbon reactions is a decrease in self-poisoning by coke. As described previously, the latter is thought to form by polymerization of acetylenic residues (50) which are associated with larger contiguous-site arrays (61).

The above examples serve to illustrate the marked effects which alloying or bimetallic cluster formation can have on hydrocarbon reactions.

E. THE APPLICATION OF BIMETALLIC CATALYSTS FOR THE CATALYTIC CONVERSION OF COAL

The important reactions involved in the catalytic conversion of coal are listed in Table 1, with examples of metals which catalyze these

# TABLE II-1

## EXAMPLES OF METAL-CATALYZED REACTIONS

| REACTION | TYPICAL METAL CATALYSTS | HIGH ACTIVITY METALS |
|---|---|---|
| **Hydrogenation** | | |
| - Aromatics | Group VIII, Mo, W, Re | Pt, Rh, Pd |
| - CO | Group VIII, Cu, | Ru, Fe, Ni, Co |
| - $CO_2$ | Co, Fe, Ni, Ru | Ru, Ni |
| **Dehydrogenation** | Group VIII | Pt, Pd |
| **Dehydrocyclization** | Pt, Pd, Ir, Rh, Ru | Pt, Ir |
| **Hydrogenolysis** | | |
| - C-C Bonds | Group VIII, Re, W, Mo | Ru, Ir, Ni |
| - C-N Bonds | Group VIII, Re, W, Mo, Cu | Ni, Pt, Pd |
| - C-O Bonds | Group VIII, Re, W, Mo, Cu, Ag | Pt, Pd |
| - C-S Bonds | Group VIII, Re, W, Mo, Cu, Ag | Pt, Pd, Rh |
| **Isomerization** | | |
| - Double Bond Shift | Group VIII | Pd, Pt |
| - Skeletal | Pt, Ir, Pd, Au | Pt |
| **Water-Gas Shift** | Group VIII, Cu, Ag | Pt, Rh, Fe |

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reactions. It is useful to consider in at least a broad sense, how bimetallic catalysts might impact in these areas. This can then serve as an introduction to the more specific and detailed treatment of this subject for the various processes discussed in Part 3 of this study. Before discussing any of the reactions listed in Table 1, it should be re-emphasized that metallic catalysts in general are not expected to survive as metals in a coal liquefaction environment with sulfur levels of greater than 1 percent. As shown previously (25), all metals can form bulk sulfides under these conditions, and therefore the true catalyst would be a mixed sulfide and not a bimetallic system. This means that one cannot take advantage of the catalytic properties of bimetallic catalysts, which inevitably depend upon the metallic properties of these systems, for the direct liquefaction of coal to boiler fuel. However, as discussed elsewhere (25), the concepts uncovered in the evolution of many new bimetallic catalysts may find use in preparing supported highly dispersed mixed sulfides and oxysulfides. In discussing the applications of bimetallic catalysts to pertinent reactions, it is convenient to divide these reactions in a way similar to that for Table 1.

### 1. HYDROGENATION/DEHYDROGENATION

The primary applications for bimetallic catalysts in this category fall in two areas, upgrading or refining of processed (low-sulfur) coal liquids to refined fuels, and $CO/H_2$ synthesis reactions. The refining processes of interest include hydrocracking, naphtha reforming, and skeletal isomerization. Each of these processes require a delicate balance between hydrogenation activity and support acidity to minimize gas make and coke formation, and thereby to

maximize the yield of liquid products. One cannot draw directly on data for processing petroleum feedstocks which usually have substantially different processing characteristics than those for coal liquids. However, many of the basic concepts, procedures, and preparative techniques which have been developed for bimetallic systems, and which have led to the discovery of new catalysts with low hydrogenolysis activity, low coke yields, and increased thermal stability, should find application in coal upgrading processes. Studies are needed of supported bimetallic catalysts with variable hydrogenation/acidity ratios for both model reactions and real feeds. Hydrocracking is perhaps most important in this respect. Work in this area should also include studies of catalyst regeneration by oxidative procedures. Studies of the interaction of $H_2S$ with multimetallic catalysts are also needed. There is some evidence (46) to suggest that at lower levels of sulfur (say 0.1%), bimetallics offer increased sulfur tolerance. This needs to be verified, explored, and developed.

In the $CO/H_2$ synthesis area (Fischer-Tropsch synthesis), primary problems have been product selectivity, sulfur sensitivity, and deactivation by sintering and carbide formation. Recent work (62, 63) has shown that the binding energy of $H_2$ and CO to the metal surface can have a strong effect on the $CO/H_2$ synthesis reaction. It is known (64) that alloy or cluster formation can affect this energy, and therefore it would be expected that this might lead to controlled product selectivity. As previously discussed, decreased sulfur sensitivity and increased stability with respect to sintering are also expected for bimetallic systems.

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## 2. HYDROGENOLYSIS

Hydrogenolysis of C-C bonds has already been discussed in detail. It can be controlled to minimize gas make or coke formation. This work is likely to find applications in both upgrading coal liquids and in $CO/H_2$ synthesis. For the latter, decreased hydrogenolysis activity for Ni, Ru, or Co by bimetallic formation may lead to lower methane yields, a shift in product distribution to liquids, and lower coke formation.

The hydrogenolysis of C-N bonds has received very little study and, as discussed in Section VII, is an area where more work needs to be done. If, as is the case for C-C hydrogenolysis, the rate limiting step of the reaction is C-N scission, bimetallic systems which optimize the interaction of carbon and nitrogen with the metallic surface will be of interest. Much work remains to be done in this area.

Carbon-oxygen hydrogenolysis is a very facile reaction, almost unavoidable in coal processing and a consumer of hydrogen. The applications of bimetallic systems in this area are not clear at this time.

The reaction of C-S bonds (desulfurization) is of course a primary reaction in coal processing. However, as discussed in Part 2, oxides, sulfides, and oxysulfides as well as a number of other nonmetallic materials are likely to be most important for this reaction. Even though metals are active for this reaction, at sufficiently high sulfur levels sulfidation of the metal probably occurs.

### 3. <u>WATER-GAS SHIFT</u>

The water-gas shift reaction is usually catalyzed by complex oxide systems such as $ZnO \cdot Cr_2O_3$ and $ZnO \cdot CuO$ (65). The reaction is also catalyzed by metals, however in some instances there can be severe deactivation with a zero-valent metal catalyst due to facile catalysis of the Boudouard reaction:

$$2CO \rightleftharpoons C + CO_2$$

This reaction can cause substantial carbon deposition on the catalyst. This is very evident with iron oxide catalysts which have reasonable activity for the water-gas shift reaction. If the $H_2O/CO$ ratio is reduced to sufficiently low values, the oxide is reduced to metallic iron and deactivates rapidly because of carbon deposition by the Boudouard reaction. Similar effects are expected for other metals. Therefore, unless other components were included in the catalyst to minimize carbon deposition, one would expect metallic or multimetallic catalysts to readily deactivate. There is a positive aspect of the use of metals for the water-gas shift reaction. Multimetallic systems provide a mechanism for altering the surface bond strengths of CO and $H_2$, and therefore give control over the rate-limiting step (66). However, as will be discussed in Part 2 of this study, this is also possible with complex oxides which are not active catalysts for the Boudouard Reaction, and therefore not as readily deactivated.


### F. <u>SUMMARY</u>

Bimetallic catalysts represent an important chapter in the development of heterogeneous catalysis. Studies with these materials have played a major role in increasing our understanding of the electronic

and geometric factors in catalysis by metals. The necessity for differentiating between surface and bulk compositions in such work cannot be over-emphasized. Failure to do so may seriously affect the conclusions concerning the catalytic properties of these systems.

Significant progress has been made in the preparation and characterization of bimetallic catalysts. A major factor in this work has been the development of improved characterization techniques for surface analysis, including selective chemisorption, Auger spectroscopy, and photoelectron spectroscopy. All of these techniques at present have limitations, but used in conjunction with each other they do give important information for understanding bimetallic catalysts.

It is clear that bimetallic catalysts have potential applications for a number of coal processing steps which do not involve high sulfur concentrations. The development of these materials over the last five to ten years has led to catalysts with controlled activity and selectivity, increased thermal resistance and activity maintenance, and a potential for improved sulfur resistance. The applications which have been briefly mentioned in this last section will be treated in some detail for the specific processes outlined in Part 3 of this study.

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