II. INORGANIC CHEMISTRY

A. INTRODUCTION

Inorganic chemistry is a subject that covers a large number of topics related to inorganic and organometallic materials. Several of these, in particular preparation and characterization, have been discussed in Part 1 and will not be pursued here. The purpose of this section is to review and analyze the impact of new compositions of matter on catalysis over the last decade, and to identify the classes of materials which have the greatest potential for the discovery of new catalytic materials. This analysis takes into account the problems and conditions of coal conversion.

Inorganic chemistry has contributed to catalysis in two ways. In the broadest sense, the synthesis and characterization of new materials has provided an enormous wealth of interesting compounds with new compositions and properties. In addition to exploring the limits of binary stoichiometries, a large number of ternary or higher compounds have been reported, thus extending the range of properties applicable to catalytic phenomena. Secondly, and more specifically, the solid state chemistry of materials has been used with increasing frequency in the last decade to solve catalyst problems such as thermal stability, chemical stability in reactive environments, and the stabilization of oxidation states with desired catalytic properties.

In the present section, a general overview of the most important families of compounds will be presented. Properties of interest to catalysis will be highlighted, and some of the applications discussed, in particular as they relate to coal conversion.

B. SCOPE OF INORGANIC CHEMISTRY

A look at the materials studied in solid state and inorganic chemistry is, in effect, a look at the periodic table of the elements. The combinations are innumerable. The wealth of materials is expanded even further due to the ability of many elements, in particular the transition metals, to exhibit a large number of valence states. In spite of the vast number of compounds, there are groups of materials which exhibit common properties, thus making it possible to obtain an overview of their chemistry.

The most important families of compounds are shown in Table II-1. Of these, only a limited number have been considered for catalytic applications. Furthermore, among the groups that are used as catalysts (oxides and metals, in particular), there are still large numbers of compositions that have not been explored. Some of these will be highlighted in the following discussion. The properties of the various groups will be summarized, and the variation in these properties between the members of a group noted. For a more detailed discussion of the properties of a large number of catalytically interesting materials, the reader is referred to an earlier study (1). One class of materials, multimetallic alloys and clusters, has been discussed in detail in Section I of Part 1. These materials are therefore mentioned only briefly in the following discussion.

1. OXIDES

Metal oxides constitute a very large class of compounds. They are important catalytic materials, and are used in a number of industrial processes. A few representative examples are shown in Table II-2.

TABLE II-1. SCOPE OF INORGANIC CHEMISTRY PERTINENT TO COAL CONVERSION CATALYSIS

Class of Compounds	Occurrence	Typical Stoichiometries (1)	Typical Examples (Structures)	General Comments and Areas of Potential Application in Coal Conversion
Oxides				
Simple	All Metals	M_3O MO_4	Cs_3O Al_2O_3 (2)	Thermal and chemical stability except in high H_2S concentrations for certain compositions
Complex	All Metals	Extensive	$CuFeO_2$ $PtCoO_2$ $FeTiO_3$ (Ilmenite) $NiCrO_3$ (Corundum) $BaTiO_3$ (Hexagonal) $SrTiO_3$ (Perovskite) $CrVO_4$ (Rutile) $NiWO_4$ (Wolframite) $Eu_2(WO_4)_3$ (Schoelite) $Ni2Al_2O_4$ (Spinel) Al_2TiO_5 (Pseudobrookite) $Se_2Ti_2O_7$ (Pyrochlore) $Fe_3Al_2(SiO_4)_3$ (Garnet) $NaWO_3$ (Bronze) $Mg_2Mo_3O_8$	Multiplicity of oxidation states Interesting precursors for HDS catalysts New compositions for water-gas-shift, in particular compounds with metal clusters Variable acidity of interest for coal liquefaction
Sulfides				
Simple	All Metals	M_3S MS_4	V_3S (β-Tungsten) VS (Nickel-Arsenide) V_2S_3 V_3S_4 V_5S_8 VS_4 MoS_2	Thermal and chemical stability, in particular in H_2S Interesting defect chemistry that may be important for catalytic activity Complex sulfides offer new compositions of interest, containing cations of known catalytic activity Possible HDS catalysts if synthesized in high surface area

(1) Emphasis on metals, (M)
(2) These are just two examples of a large variety of structures and stoichiometries.

TABLE II-1 (Cont.)

Class of Compounds	Occurrence	Typical Stoichiometries	Typical Examples (Structures)	General Comments and Areas of Potential Application in Coal Conversion
Complex Sulfides	All Metals	Extensive	$BaZrS_3$ (Perovskite) $FeCr_2S_4$ (Thiospinel) $ZnAl_2S_4$ (Thiospinel) $Al_{0.5}Mo_2S_4$	
Carbides				
Simple	Grps. I-IV, Fe, Co, Ni	M_4C MC	Mn_4C Fe_3C (Cementite) W_2C WC_{1-X}	Interstitial compounds, refractory, metallic, and hard High thermal stability
Complex	Metals	Extensive	Mo_3Al_2C (β-Manganese) Pd_3AlC (Perovskite) Pt_3SnC (Perovskite) Pt_3PbC (Perovskite) $W_{16}Ni_3C_6$ (K-Carbide) V_2AlC (H-Phase)	Unstable in high H_2S concentrations, but certain compositions likely to be stable in low H_2S concentrations Potential for methanation, where carbiding is a problem Complex carbides likely to retain metal characteristics, but with increased thermal stability
Nitrides				
Simple	Same as Carbides	Same as Carbides	Ti_2N V_2N TiN VN Ta_3N_5 Co_3N_2	Interstitial, similar to carbides High thermal stability, refractory and hard Unstable in high H_2S Concentrations More stable than carbides in low H_2S concentrations Have been explored for Fischer-Tropsch, however no clear evidence of unusual behavior

TABLE II-1 (Cont.)

Class of Compounds	Occurrence	Typical Stoichiometries	Typical Examples (Structures)	General Comments and Areas of Potential Application in Coal Conversion
Complex Nitrides	Metals	Extensive	V_3Zn_2N (β-Manganese) Ni_3AlN (Perovskite) Ti_2AlN (H-Phase)	Less refractory structures of interest for HDN
Borides Phosphides Silicides	All Metals	M_3B MB_{12}	Ni_3B (Isolated B Atoms) MoB (B Chains) VB_2 (B Layers) CrB_4 (3D Boron Frameworks) $Co_{21}Hf_2B_6$ (Perovskites)	Like carbides and nitrides, high thermal stability Thermodynamic evidence for sulfur resistance in high H_2S concentrations, in particular Group VIII
		M_2P MP_4	Co_2P (Isolated P Atoms) VP FeP_2 (P_2 Groups) CdP_4 (Phosphorous Layers)	Interesting for methanation Possibly resist carbiding, in particular Group VIII Will not resist oxidizing environment at high T.
		M_3Si MSi_3	Mo_3Si (Isolated Si Atoms, βW Struct) TiSi (Chains) $TiSi_2$ (Layers) $SrSi_2$ (3D Networks)	
Alloys and Multi-Metallics	All Metals	Extensive	Cu_3Pt (ordered only with Ni_3FC long annealing times) FeSW (Nickel Arsenide Struc) Cu_3Al (Hume-Rothery Electr. CoAl compound, Engel- CuZW Brewer correlations) $ZrPt_3$	Ability to obtain gradual change in properties or dramatic changes in selectivity patterns Certain intermetallic compounds likely to exhibit high thermal stability All metals unstable in high H_2S Possible H_2S resistance of alloys at low H_2S Definite potential for improved methanation

TABLE II-1 (Cont.)

Class of Compounds	Occurrence	Typical Stoichiometries	Typical Examples (Structures)	General Comments and Areas of Potential Application in Coal Conversion
Organo-Metallic	--	--	$Ni_4(CNC(CH_3)_3)_7$ (Ni Clusters) $Rh_4(CO)_2$ (Rh Clusters) $Pt_3(CN)_6(C_4H_9)_6$ (Pt-Pt bonds)	Well characterized reactive centers, high activity and selectivity Anchoring on high surface area supports possible Unusual and controllable metal-metal bonds Maximum availability of active center, however, poor thermal stability Some indications of sulfur tolerance, but unconfirmed Precursors for synthesis of supported catalysts Clusters show interesting activity patterns Possibility of CO/H_2 synthesis by clusters an important aspect of the application to coal conversion

TABLE II-2

REPRESENTATIVE REACTIONS CATALYZED BY OXIDES

Reaction	Catalyst
Partial Oxidation	CoO-MoO_3 V_2O_5
Oxidative Dehydrogenation	Bi_2O_3-MoO_3
Cracking	Zeolites
Reforming	Al_2O_3 (Acid Function)
Polymerization	MoO_3/Al_2O_3
Water Gas Shift	$CuO + ZnO$-Al_2O_3 Fe_3O_4-Cr_2O_3
Methanol Synthesis	CuO-ZnO-Al_2O_3

Oxides exhibit a large number of structures and compositions. The examples shown in Table II-1 are only representative of an extensive and complex chemistry. Some of the main properties of these oxides are reviewed in this section.

a. Thermal Stability

In general, oxides exhibit high thermal stability at the temperatures and environments of interest to catalysis. Some exceptions are the oxides of the noble metals such as those for Os or Ru, which form volatile species at low temperatures. This eliminates the use of these materials in oxidizing environments. Under most conditions, however, oxides maintain high surface areas up to temperatures approaching 1000°C. For this reason, several of them (such as Al_2O_3 and SiO_2) are routinely used as catalyst supports. Certain environments, however, are damaging to the stability of oxides. Steam, in particular, leads to crystal growth and agglomeration at elevated temperatures, as a result of the well known role which water plays in sintering and chemical vapor transport (2). This puts a constraint on the use of steam in certain processes at elevated temperatures.

b. Chemical Stability

The chemical stability of oxides varies across the periodic table. This is particularly evident when one examines the behavior of various oxides in an H_2S environment, especially at elevated temperatures (1). Three degrees of stability can be distinguished. The most stable oxides include those of Al, Si, and the alkaline earth metals, Be and Mg (1). The oxides of the rare earth elements as well as those of Group IV (Ti, Zr, Hf) show intermediate stability. All other transition metal oxides are thermodynamically unstable in H_2S. It should be stressed, however, that the criteria of stability depends on the severity of the environment (e.g. temperature, pressure, H_2 and H_2S

partial pressure). There is a direct relationship between the free energy change and the pressure of H_2S. For the above classification, the high H_2S concentrations expected in coal liquefaction ($\sim$1%) were used. However, the relative trend remains the same for lower concentrations. It is not surprising, therefore, that oxide catalysts are susceptible to H_2S poisoning, as observed in shift and methanol synthesis. Support materials such as oxides of Al and Si, on the other hand, are stable even in the most severe H_2S environments.

The same conclusions can be drawn in a reducing environment. A look at the free energy changes for the reduction of different transition metal oxides shows that the reducibility increases as one progresses to the right of the periodic table (1). This trend persists through the Group VIII metals. Thus, the reducibility trend in the first series is $Fe \ll Co < Ni$ (3).

c. Other General Properties of Catalytic Interest

As illustrated in Table II-2, oxides have been used extensively in catalysis. Properties of particular interest are surface acidity, which can be varied over several orders of magnitude (5-7), and the ability of oxides to exchange lattice oxygen with gaseous O_2 (8). The former is used in the petroleum industry extensively for cracking and reforming (1), while the latter is a property that relates to the ability of oxides to catalyze partial oxidation of hydrocarbons (9).

As can be seen from the examples in Table II-1, complex oxides offer a wealth of compositions and structures. Many of these have received only limited attention in catalysis. To illustrate the variety in the structure of complex oxides, it is of interest to examine the difference between two cases of catalytic interest: spinels and perovskites. In spinels, the basic structural unit is a close packed network of oxygen atoms. The metal ions reside in the tetrahedral and octahedral interstices formed by this network. The type of site occupied depends roughly on the size of the cation (1). In general, spinels are thermally very stable and exhibit a range of compositions that depend on the extent of the occupation of interstitial sites. Typical examples are $CrAl_2O_4$ (ruby) and $MgAl_2O_4$ (the mineral spinel). In perovskites, on the other hand, one of the metal cations of the complex oxide is too large to fit in the interstitial sites. This metal becomes part of the close packed network, with a metal to oxygen ratio of 1:3, while the other smaller cations again reside in octahedral oxygen interstices. The interesting feature of this structure is the ability to exist with less than stoichiometric amounts of the large cation, leaving a rather open structural network. One extreme case is WO_3, where all the sites available to large cations such as Li, Na, K and Rb are empty. The structure is nevertheless stable, and even admits smaller ions such as H^+. This ability to exist in a number of stoichiometries allows for practically continuous variations in oxidation states, and therefore continuous changes in the electronic properties of the solid.

The large number of compositions and structures result in complex oxides with a variety of electronic and chemical properties. These are likely to be reflected in changes in surface properties which may prove to be of catalytic interest. In the perovskite structure, cations of transition metals are located in unique and unusual environments. Certain oxides, for example, exhibit smaller metal-metal distances than encountered in the element itself, ($BaRuO_3$ with a Ru-Ru distance of 2.55 Å (10)) or clusters of several transition metals ($MgMo_3O_8$, with Mo_3 clusters (11)). The catalytic properties of such interesting compositions have not been studied in detail. However, they have been applied in certain cases to solve specific problems. The $BaRuO_3$ system provides an example of such an application. It has been known for some time that ruthenium is one of the most effective NOx reduction catalysts, in particular because of minimum NH_3 formation (12). It cannot be used as an automotive exhaust control catalyst, however, because it encounters oxidative conditions which volatilize the ruthenium as RuO_4. To stabilize the ruthenium during oxidation, Shelef and co-workers prepared the metal as a complex oxide with alkaline and rare-earth elements (13). Under oxidizing conditions, the elements form the above mentioned ruthenate. Under reducing conditions, the stable state is a two phase system consisting of Ru metal and the alkali or rare-earth metal oxide. The solid state chemistry of the ruthenium-alkaline earth system, therefore, lends itself ideally to the solution of the thermal stability problem of ruthenium. Under oxidizing conditions, a stable, non-volatile complex perovskite is formed. Under reducing conditions, the zero valent metal is "regenerated" and available to perform its catalytic function.

This example is an excellent illustration of the impact that the understanding of the inorganic chemistry of materials can have in catalysis.

d. Zeolites

One family of oxides that deserves special attention in the context of this overview of inorganic chemistry is zeolites. They have been used in many catalytic reactions, their synthesis and solid state chemistry studied extensively over the last decade.

Zeolites are members of a large class of compounds called silicates. They consist of SiO_4 units partially substituted by Al ions with positive ions such as Na^+ or K^+ to compensate for the charge imbalance between Al^{3+} and Si^{4+}. The SiO_4 units are combined in the structure by sharing faces, edges, or corners. In the case of zeolites, the units share only corners. In doing so, they form open structures with cavities and channels of varying sizes. This unusual structure is largely responsible for many of the interesting properties of these materials.

Naturally occuring zeolites display fibrous structures like edingtonite ($Ba(Al_2Si_3O_{10}).4H_2O$), lamellar structures such as phillipsite ($(K, Na)_5\ Si_{11}\ Al_5O_{32}\cdot 10H_2O$), and zeolites with 3-dimensional polyhedral cavities such as chabazite ($Ca(Al_2Si_4)O_{12}\cdot 6H_2O$) (14). The zeolites with polyhedral cavities have found greatest application in catalysis. They can be synthesized with controlled cavity and channel sizes, thereby providing a considerable variation in physical properties. However, it is the chemistry of these materials, and in particular their acidic properties, which is largely responsible for their extensive use in catalysis since their introduction as fluid cracking catalysts in 1962 (15).

Since many of the properties that make zeolites such interesting materials are closely associated with their structure and chemistry, they represent a good example of the impact of inorganic chemistry on catalysis. The most interesting aspect of this inorganic chemistry is the <u>synthesis</u>, since it determines the <u>structure</u> and <u>size</u> characteristics of the zeolite. In this respect, the type of hydrated cations present in the starting gels is important (16). In general, the more open zeolite structures are prepared from sodium rather than potassium-containing gels. This is a direct function of the size of the hydrated ion, since the tetrahedral building blocks of the zeolite are believed to surround this hydrated ion during synthesis (16).

Another important aspect is the stability of the zeolite which is a function of composition. For example, zeolites which substitute germanium for silicon ions are considerably less stable (17). On the other hand, it has been recently reported that Si-Al zeolites which are deficient in aluminum tolerate severe hydrothermal conditions (18, 19). Similarly, the greater Si-Al ratio in Y zeolites compared to X zeolites gives the former much greater structural stability.

The acidity of zeolites is a property of great interest to catalysis. It depends on a number of factors that are related to the inorganic chemistry of these compounds. It is primarily controlled by the types of ions present in the structure which compensate the imbalance between Al^{3+} and Si^{4+}. Zeolites with univalent cations (e.g. Na^+, K^+) have low acidity. Ion exchange of these materials with ions such as Ca^{+2}, Mg^{+2}, Sr^{+2}, and Zn^{+2} leads to an increase in the acidity, with a distribution concentrated towards strong acid sites (20, 21).

In addition to their variable acidity, zeolites have shown evidence for much greater poison resistance to H_2S and NH_3 than conventional amorphous silica-alumina cracking catalysts (1). The source of this higher resistance is not well understood. However, it has important implications in a number of industrial processes, in particular in coal conversion since both H_2S and NH_3 are present. The adsorption of these compounds can affect the acidity of zeolites, thus leading to changes in the selectivity of these catalysts.

Finally, there is an aspect of zeolites which has been recognized only recently and may have interesting catalytic consequences: the presence of metal catalyst-zeolite interactions. First observed for Pt exchanged into a Y zeolite (22), and since confirmed for Rh and Pd (23), the small metal clusters in the zeolite cages are found to be electron deficient. This is concluded from ESR spectra (23) as well as the catalytic behavior of the system (22, 24). In the case of platinum (22), the activity is more typical of iridium, its neighbor in the periodic table. This ability to modify activity by varying the electronic interaction with the zeolite support is an important aspect of these materials. In fact, as pointed out by Dalla Betta and Boudart (22), it has implications for the sulfur resistance of these catalysts in addition to the observed changes in catalytic activity.

2. SULFIDES

Formation of transition metal sulfides is particularly important in the synthetic fuels area. Many of the reactions are carried out in high concentrations of H_2S, and therefore require catalysts that survive such environments. This is particularly true for hydrodesulfurization. In other reactions, the problem of sulfur tolerance is also severe, as was discussed in detail in Section VI-C of Part 1. It is likely that many catalysts are in the sulfided or partially sulfided state during reaction. The study of sulfides is therefore an important aspect of a general review of materials.

In spite of their importance, only few sulfides have been tested as catalysts. They have been used primarily for hydrogenation reactions, in particular when sulfur-containing compounds are present. In general, the catalysts tested are mixed sulfides of Ni, Co, W, and Mo (25). Only limited information is available on the structure of these materials at reaction conditions. However, a detailed study of the Ni-W sulfide system by Voorhoeve et al. (26) has shown that the interaction between the nickel and the WS_2 matrix has an important effect on the catalytic activity. This suggests that complex sulfides should be explored more extensively for catalytic applications, in particular in view of the growing interest in these materials in the solid state chemical literature (27, 28, 29). The properties of sulfides will now be discussed briefly.

a. Thermal Stability

The examples shown in Table II-1 illustrate the large number of stoichiometries possible for one transition metal sulfide. This behavior of vanadium is typical of a large number of metals. In addition to various compositions, metal sulfides often exhibit extensive homogeneity ranges (e.g. $VS \rightarrow V_5S_8$). The thermal stability of a particular composition is a sensitive function of sulfur pressure. A discussion of the thermal properties of sulfides is therefore closely related to the chemical environment of the system.

The thermal chemistry of a number of metal sulfides was studied as early as the 1930's. For vanadium, for example, Biltz and co-workers investigated a broad range of compositions at various sulfur pressures (30). These studies were followed by extensive work of French workers in the laboratory of Tridot (31, 32) who followed the decomposition of vanadium sulfides gravimetrically. Except for the German and French investigations, however, there has not been much work in this area. In particular, thermal data is lacking at the low sulfur concentrations of interest in most catalytic systems.

In spite of this lack of data, the general evidence is that the lower sulfides such as CoS and VS are stable to high temperatures. VS, for example, has been reported at temperatures as high as 1500^{o}C in vacuum (33). By contrast, stoichiometries such as VS_4 decompose at temperatures as low as 300^{o}C even in the presence of high sulfur pressures (31, 32). This low stability explains, for example, the decomposition of VS_4 catalysts tested for hydrogenation and desulfurization (34). This illustrates the importance of the study of the thermochemistry of these compounds if they are considered for catalytic applications.

b. Chemical Stability

The stability of sulfides in H_2S is a function of pressure and temperature. As discussed extensively in reference 1, in the case of H_2S the important parameter is the equivalent (or "virtual") sulfur pressure which is in equilibrium with an H_2S/H_2 mixture. This parameter is also important in determining the possibility of sulfide formation for other materials. For metals, for example, the minimum H_2S concentration for bulk sulfide formation can be calculated from free energy data (1). A few examples are shown in Table II-3. It can be seen that the sulfiding tendency of transition metals varies widely. In general, as discussed in Section I of Part 1, all transition metals will sulfide in the high H_2S concentrations of coal liquefaction. The reaction therefore proceeds in the presence of a metal sulfide. At lower H_2S concentrations, however, this will not be the case. At conditions of methanation, for example, ($H_2S < 1$ ppm) sulfide catalysts such as NiS will be unstable. However, considerable interaction of H_2S with the surface can still occur.

The above observations apply to an H_2S/H_2 environment. Several sulfides (such as MnS or VS) are stable in very low H_2S pressures or, in the limit, in vacuum. However, most sulfides will oxidize in the presence of O_2 (1). This is an important aspect of the chemical stability of these materials because many catalytic processes use oxidative regeneration procedures. In such circumstances the balance between the oxide and sulfide becomes important and the possibility exists of partial sulfidation - namely the formation of oxysulfides. There is little information on these important materials. This is an area that requires more research, in particular when

TABLE II-3

MINIMUM CONCENTRATION OF H_2S (AS PERCENT H_2S IN H_2) REQUIRED FOR BULK SULFIDATION; T = 700 K

Stoichiometry	Concentration, %
CrS	4×10^{-4} (4 ppm)
MnS	2×10^{-11}
FeS	7×10^{-2} (700 ppm)
CoS	3×10^{-2}
NiS	2×10^{-1}
RuS	1×10^{-6} (10 ppb)
OsS	2×10^{-2}
PtS	1.3
CuS	73

oxidative regeneration is considered. The oxidation of both bulk and supported sulfides should be studied. The latter is especially important because the chemical behavior of supported systems may be different from that of the bulk, as has been suggested for cobalt molybdate HDS catalysts (35).

c. Compositions of Interest

Like oxides, there are a number of complex sulfides that result from the versatile chemistry of transition metals. Many of the properties and structures of these compounds have been studied recently. The layered structure of a number of disulfides leads to a large number of complex sulfides that resemble intercalation compounds, such as FeV_2S_4, $TiCr_2S_4$, $CuCrS_2$ (36, 37). Compounds that have the perovskite structure MM^1S_3 (M = Sr, Ca, Pb; M^1 = Zr, Ti) have also been synthesized and studied (38). Complex sulfides that incorporate a rare earth metal (such as La_4NiS_7 and $La_2Fe_2S_5$) are another group of sulfides which has received recent attention (39). Finally, sulfospinels have been investigated (40, 41), and exhibit the same non-stoichiometry shown by oxides. $Al_xMo_2S_4$, for example, has been prepared with values of x as low as 0.5. The latter stoichiometry exhibits unusual molybdenum clusters similar to some of the complex oxides discussed above. These are just a few examples of the wealth of complex sulfides that have been synthesized and characterized in the last few years. Many of them contain cations which are known to exhibit catalytic activity in a sulfide matrix, such as Mo^{4+} and Ni^{2+}. They are therefore interesting candidates for the catalytic conversion of coal in the presence of strong sulfiding environments, and will be discussed in this respect in Part 3.

3. CARBIDES AND NITRIDES

As outlined in detail in a recent review (42), carbides and nitrides of transition metals show similarities in many of their chemical and physical properties. The structures of these materials, in particular, are closely related. Because of the large difference in size between transition metals and C or N (a factor greater than 1.7), the non-metal occupies interstitial sites formed by close packing of transition metal atoms. The presence of the non-metal in these sites substantially modifies the properties of the parent transition metal. Some of these changes are discussed in this section.

a. Thermal Stability

Carbides and nitrides are known to be refractory compounds because of their stability at very high temperatures. Thus, several carbides and nitrides melt or decompose above 3000°C and TaC has the highest melting point known for any material (about 3983°C) (43). This stability of bulk carbides and nitrides is likely to persist when these materials are prepared in fine dispersion, since carbides are known to resist sintering. In fact, metallurgists have had to add binders such as cobalt to achieve dense "cemented" carbides (using powder metallurgical procedures) for cutting tools (44). Carbides and nitrides are therefore an interesting class of materials in terms of their potential application to such exothermic reactions as methanation and Fischer-Tropsch where sintering is a severe problem.

b. Chemical Stability

The resistance of carbides such as WC to attack by severe environments is well known, and is one of the reasons why this compound has been tested as a battery electrode (45).

In the presence of O_2, however, the thermodynamic stability of these compounds indicates that carbides and nitrides will oxidize (1). Kinetically, of course, this oxidation does not take place at low temperatures. However, at temperatures of regeneration, oxidation may be a problem in the use of these materials as catalysts. This aspect requires further investigation.

In the presence of sulfur containing compounds, thermodynamic calculations indicate that most carbides are expected to sulfide (42). The sulfur level at which this occurs, and the rate of sulfidation, have yet to be determined experimentally. The same is true, in general, for nitrides. However, the most stable nitrides, such as TiN, show a positive free energy of sulfide formation, and are therefore expected to survive even in severe sulfiding environments (42).

It is interesting to note, with respect to the sulfur reactivity of these compounds, that formation of a strong refractory material does not necessarily improve sulfur tolerance. Tungsten, for example, will react with H_2S according to the equation:

$$W + 2H_2S \rightleftharpoons WS + 2H_2$$

The free energy change in this reaction at 700 K is -16.7 kcal mol^{-1} (1). For the carbide, on the other hand, the reaction

$$WC + 2H_2S \rightleftharpoons WS_2 + CH_4$$

has a free energy change of -25 kcal mol^{-1} (1). The main reason for the increased tendency of WC to sulfide in the presence of H_2S in this example is the formation of CH_4.

c. Structures and Compositions of Interest

With the exception of several Group VIII noble metals (Ru, Rh, Pd, Ir, and Pt), all transition metals form a number of carbide and nitride stoichiometries (43). They follow the empirical rules postulated by Hagg in 1931: if the radius ratio of non-metal to metal is less than 0.59, the compounds formed have a simple, interstitial structure (1). In addition to such binary compounds, a number of very interesting multimetallic carbides and nitrides have been synthesized. Of particular interest are the Nowotny octahedral phases (43). They contain two or more transition metals, and display complex structures, many of them bearing a relationship to the oxide structures discussed earlier. Some examples are shown in Table II-1. Particularly interesting are the carbide and nitride perovskites such as Pt_3ZnC (1). These compounds are likely to show interesting modifications of the bulk properties of the parent metals which in turn should be reflected in the surface chemistry of these materials.

In addition to the interesting carbides and nitrides mentioned above, carbonitrides and oxide-carbides are formed by many transition metals (46). This presents new opportunities for the synthesis of novel compounds with a broad range of physical and chemical properties. As discussed in Part 1, the synthesis of these materials in high surface areas is a key challenge to their application in catalysis. Efforts in this direction are currently being undertaken in only a few materials science laboratories (47). In general, the attention of materials scientists has been focused on the preparation of dense materials. However, techniques of powder metallurgy are likely to have a bearing on the synthesis problems discussed above.

4. BORIDES, SILICIDES, AND PHOSPHIDES

Like carbides and nitrides discussed above, borides, silicides, and phosphides display many similarities in structure and properties (1, 5). It is therefore useful in a general overview to discuss them together.

Borides, silicides, and phosphides are formed by most metals. The occurrence of these compounds is, in fact, more extensive than carbides and nitrides since even the Group VIII noble metals form a number of stoichiometries with Bi, Si, and P. However, these compounds have not been studied as completely, in particular in terms of their thermochemical properties.

Some of the more outstanding characteristics of borides, silicides, and phosphides are high thermal stability, strength, chemical stability, and structure.

a. Thermal Stability

Borides and silicides display thermal stabilities that are almost as high as the carbides and nitrides discussed above (e.g. TiB_2 melts at 2980°C). Those elements that form the most stable nitrides are also expected to form phosphides with melting points above 2200°C (48), although little work has been done with these materials.

While the stability of carbides and nitrides varies quite sharply across the periodic table (decreasing as one approaches Group VIII), silicides and borides do not show such dramatic variations. As indicated above, the latter elements form stable binary phases even with the noble metals of Group VIII. This presents the possibility of modifying the catalytic properties of the Group VIII metals, which are of primary importance in catalysis. This aspect will be discussed later.

b. Chemical Stability

A comparison of the enthalpies of formation of borides, silicides, and phosphides with those of oxides shows clearly that the former tend to oxidize in the presence of O_2. However, in practice these compounds, and in particular the silicides, have shown very high resistance to oxygen attack (49). They are used as heating elements because of this property. As pointed out by Searcy (49), this chemical resistance is likely to be the result of a coating of SiO_2 which protects the compound from bulk oxidation. However if the metal silicide is the important catalytic material, this coating would also lead to a decline in activity.

The most interesting chemical property of this group of materials becomes evident upon examination of the thermodynamics of sulfidation. As expressed earlier, the thermochemistry of these compounds has not been studied very extensively. For borides, in particular, there is only limited data for certain compositions of the Group IV metals (50). Data for silicides is more general. However, it varies by as much as 30% between different laboratories (49). In spite of this uncertainty, a definite trend is apparent (1): as one proceeds to the right of the periodic table, silicides become more resistant to sulfidation. Group VIII silicides, in fact, are expected to be sulfur tolerant even in high H_2S concentrations. A similar trend is observed for phosphides, and is expected for borides in view of the similarity in other properties of these three materials (1). This has obvious implications for catalysis, and is discussed later.

c. Structure and Stoichiometry

The common feature that is most evident in the three classes of compounds discussed here is structure. The size of phosphorous and silicon is too large to form interstitial compounds of the type formed by C and N. Boron is on the borderline of the Hägg rule (35) discussed earlier for interstitial carbides and nitrides, and in general behaves more like Si and P than C and N. The structures formed are characterized by a wide range of stoichiometries, and the formation of non-metal networks at high non-metal to metal ratios. Some examples are illustrated in Table II-1.

In addition to simple compounds, a number of complex structures are also encountered. This is particularly the case for boron, which forms series of compounds such as MoCoB, WFeB, WCoB. Perovskite-like structures are also encountered. They exhibit interesting properties such as cluster formation in the case of $(Co_{13})(Co_8)Hf_2B_6$ (51).

It was mentioned earlier that borides are at the borderline of the criteria for interstitial compounds. This is confirmed by the formation of numerous borocarbides such as Mo_2BC and ScB_2C_2 (52). The latter stoichiometries, also formed by the 4f elements (lanthanide series), display close metal-metal distances and interesting B-C networks (52). They are likely to have unusual chemical and physical properties which have not been explored to date.

5. ORGANOMETALLIC COMPOUNDS

The wide scope and versatility of organometallic chemistry is exemplified by the many volumes which have been written on this subject (53-55). Organometallic complexes have been used for catalytic reactions for many years. The hydroformylation of olefins to make alcohols and the carbonylation of methanol to acetic acid using cobalt and rhodium catalysts, respectively, are two commercial examples. Therefore, in the context of the present section, these types of compounds do not represent a novel class of materials. However, organometallics deserve consideration since they have been of interest for coal liquefaction for some time. There are three reasons for this interest. First, as homogeneous catalysts they maximize contacting with coal during the liquefaction process, and therefore in principle should be more effective than heterogeneous catalysts. Second, organometallic complexes tend to be highly active, specific, and selective catalysts, and thus one would hope to minimize unwanted reactions and unnecessary hydrogen consumption. Third, it has been suggested (but yet to be domonstrated) that this class of catalysts may be more poison-resistant than heterogeneous systems. Also, there are two recent advances in organometallic chemistry which could have an impact on the applicability of this area of inorganic chemistry to catalysis; namely the synthesis of polynuclear cluster complexes and the anchoring of complexes to heterogeneous surfaces. The former promises to extend the ranges of catalytic properties for organometallic complexes and to give a greater degree of control on catalyst selectivity and specificity. The latter has been developed as a mechanism for obviating the separation problems which have been a primary constraint for the commercial development of organometallic catalysts. These two advances form the basis for the following discussion.

a. Polynuclear Organometallic Complexes

The primary interest in the synthesis of organometallic complexes with metal clusters is the possibility of new catalytic properties not exhibited by the mono-nuclear species. As pointed out in the interesting review of Norton (56), these complexes provide the opportunity to take advantage of several unique features of heterogeneous catalysts in a well defined and reproducible organometallic framework: the possibility of bonding with several metal atoms, thus leading to selectivity control; the migration of species on the catalyst cluster "surface"; and, finally, the added flexibility in achieving modifications of catalytic properties due to metal-metal interactions.

In the last few years, a number of cluster compounds have been synthesized. They range from small clusters of Pt and Ir compounds such as $Pt_3[CN(C_4H_9)]_6$ (57) and $Ir_3(CO)_{12}$ (58) to large cluster compounds of gold, $Au_{11}[P(C_6H_5)_3]_7I_3$ (59), and rhodium, $Rh_{13}(CO)_{24}H_3$ (60). While the properties of these cluster compounds are not completely understood, several interesting aspects have been determined. The mobility of some of the ligands is substantial. In (π-$C_5H_5)_2Rh_2(CO)_3$, for example, there are two types of carbonyl groups: bridging and terminal. Carbon 13 NMR, which can in principle distinguish between these two types of CO species, cannot resolve them in the case of this di-rhodium complex because of rapid rearrangement of the carbonyl groups (61). As pointed out by Norton (56), this mobility parallels the fast surface diffusion of chemisorbed species on heterogeneous materials. In addition to this rapid mobility, there are clear indications of metal-metal interactions in these clusters (56). Recent reports of the preparation of multimetallic clusters in organometallic complexes (62) therefore opens up many of the interesting phenomena that have motivated the development of the heterogeneous multimetallic catalysts described in Part 1. These observations confirm the expectation of unusual properties for these materials and the likelihood that they will exhibit interesting catalytic properties. This latter aspect of these materials has not yet been established. However, there are preliminary indications that clusters exhibit unique catalytic chemistry. This is exemplified by the work of Muetterties (63) who observed cyclization of acetylene to benzene and butadiene to cyclo-octadienes at room temperature in the presence of $Ni_4(CNC(CH_3)_3)_7$. No such reaction has been observed with the monomer which does not contain the Ni cluster network.

b. Anchoring of Homogeneous Catalysts

There are several limitations to the application of homogeneous catalysts to coal conversion (1). The most important ones are thermal and chemical stability and catalyst recovery. The former is a serious problem in liquefaction (in particular because of the high H_2S levels). In

Fischer-Tropsch and methanol synthesis, on the other hand, the presence of high CO pressures and low S concentrations are viable environments for certain organometallic complexes. The problem of separation of the catalyst from the product, on the other hand, is a general problem regardless of the type of process being considered. The problem is extreme, of course, when expensive metals are used in the organometallic complex. Unless recovery of rhodium is greater than 99%, for example, use of this metal becomes uneconomic (64). Even with less expensive metals, recovery and separation remain important challenges.

Over the last 5 to 10 years there has been an increasing effort to solve the separation problem by the reaction of the organometallic complex with a solid containing a ligand that is capable of binding to the complex. Both organic and inorganic substrates have been studied, in particular polystyrene and silicon dioxide. As discussed in several recent reviews (65, 66), the resulting "anchored" complex retains many of the important features of the homogeneous species. The carbonyl stretching frequencies in carbonyl complexes, for example, are only slightly shifted (65), and the catalytic activity and selectivity patterns of many reactions remain the same (66). However, this area is still in the early stages of development, and many problems, including complex cross-linking, have to be resolved.

c. Potential Applications

The most promising application for organometallic catalysts is the synthesis of chemicals and clean fuels from synthesis gas. The reactions in these conversions are highly exothermic, and the possibility of liquid phase catalysis offers a very efficient means of temperature control. There have been suggestions that homogeneous catalysts can be designed to be sulfur tolerant (67), however, there is no evidence to this effect in the literature except for a report of Soviet workers in the hydrogenolysis of carbon-sulfur bonds (68).

It should be recognized that while anchoring solves the catalyst separation problem, it defeats the contacting advantage one obtains with homogeneous catalysts. Also, for gas phase reactions over anchored systems, the effective heat-transfer capabilities of the corresponding liquid phase system is lost. Thus, the advantage of anchored catalysts would come in only in high catalyst utilization (effectively atomic dispersion) and unique reaction patterns due to the effect of the ligands. The latter has found an interesting application in stereospecific hydrogenation reactions. (69).

6. MOLTEN SALTS

A major problem in direct catalytic liquefaction of coal concerns achieving optimum contact between solid catalyst, gas, and liquid phases. Homogeneous catalysis has been explored with limited success in solving this problem. An alternative method is to disperse coal in a catalytic melt involving molten salts. The properties of molten salts have been detailed elsewhere (70, 71). In this section, a brief review of the properties and possible relevance of molten salts to catalysis is presented.

Upon melting, ionic salts are thought to dissociate into ions almost completely. As a result of coulombic interactions (72) each ion in the melt is surrounded by a number of appropriately charged ions. The original long range order in the salt is destroyed. Molten salts can, however, be best described by a defect solid model known as the "hole" model. Experimental data seem to support the "hole" model (71) which attributes an increase in volume from solid to fused states to the empty volumes in the salts.

The species present in melts vary for different salts. A melt of BeF_2, for example, will exhibit polymeric chains while $ZnCl_2$ forms two dimensional cross-linked layers.

Fused salts have a high capacity for solvating many materials. Gases often dissolve either by reacting or simply filling the free spaces in the melt ("hole" model). Containment of molten salts is a problem since they dissolve many other inorganic salts as well as most refractory materials. In alkali metal hydroxide melts, the presence of oxygen or water leads to the formation of peroxides which dissolve both noble metals and ceramics. In many instances fused salts also have the ability to dissolve the parent metal. The metal is highly dispersed throughout the medium, and produces metal-like properties such as increases in electrical conductivity (73). Water readily dissolves in many molten salts, especially halides. As an example, $ZnCl_2$ retains some H_2O even at $1000^{\circ}C$ (70).

The possible compositions of melts are extensive. Variations in composition give rise to systems with different melting points and very different chemical properties ranging from strong oxidizing to strong reducing, and including a wide range of acidities. This variation offers much flexibility in controlling chemical reaction conditions.

In chemical reactions involving molten salts, the melt can be considered either as a reactant, a solvent, or as a catalyst. Molten salts are especially interesting in catalysis for several reasons: possibility of dispersing solid reactants for better contacting, high thermal conductivity for heat removal, continuous regeneration or exposure of fresh catalyst surface, and high polarization forces in the melts which may affect catalytic activity and selectivity.

Only a few areas have been studied with respect to melts. Chlorination and oxidative chlorination of hydrocarbons such as methane, ethylene, and benzene have been explored using $NaCl/AlCl_3$, $NaCl/AlCl_3/FeCl_3$, and $CuCl_2$ melts (71). Other work has involved Friedel-Crafts catalytic melts such as $AlCl_3$ and $SbCl_3$ (74). Recently, Shell Oil Company has described the use of zinc halide melts as hydroconversion catalysts for heavy petroleum fractions (75, 76).

Two types of processes have been used in the synthetic fuels area. The first involves coal gasification using alkali metal carbonate or oxide melts at high temperatures such as the use of Na_2CO_3 in the Kellogg Process (77). The second is demonstrated by the use of $ZnCl_2$ and other Lewis acid halides in the Consol Process of Consolidation Coal Company (78). The latter uses molten salts for hydrocracking, desulfurization, and denitrogenation of coal and coal extract to low sulfur distillate fuel oil or high-octane gasoline. There are several problems with the Consol process, including high catalyst to coal ratios, deactivation of catalyst due to formation of ZnS, ZnO, $ZnCl_2 \cdot (NH_3)_4$ complexes, and carbon residue buildup, and the necessity of moving large volumes of corrosive materials due to large catalyst to coal ratios. It is therefore evident that while properties of moletn salts appear very interesting for catalysis, especially due to increased contact effectiveness between catalysts and reactants, there are severe problems that have to be solved before molten salts can be readily used.

C. IMPLICATIONS FOR COAL CONVERSION

The discipline of inorganic chemistry impacts in a large number of aspects of catalysis, from the synthesis of catalytic materials to the elucidation of the effect of solid state and surface chemistry on activity and selectivity. As mentioned in the introduction, the present section has emphasized the materials rather than the synthesis aspect of inorganic chemistry. In this context, innovations in inorganic chemistry may have a direct impact in a number of areas of catalysis. Three of these will be discussed with reference to the requirements and problems of coal conversion: thermal stability, chemical stability, and the more general area of unique and unusual compositions.

1. THERMAL STABILITY

It is often difficult to distinguish between thermal and chemical stability since the agglomeration of catalyst particles is influenced by the gases or liquids in the environment surrounding the catalytic material. There is therefore some overlap between this and the next section, as well as the more extensive discussion of sintering in Section III. Thermal stability is a problem in several highly exothermic coal conversion reactions such as methanation, methanol, and Fischer-Tropsch synthesis. It is also a general problem during catalyst regeneration, in particular when oxidative regeneration is used to remove carbonaceous deposits. The latter is a severe problem in liquefaction and many upgrading reactions. A number of materials discussed above and in other sections of this report show thermal properties that should be exploited in an effort to find more stable catalysts. Zeolites, refractory materials (carbides, nitrides, borides, silicides, and phosphides) and multimetallic compounds illustrate this point. In the last few years the use of zeolites as upgrading catalysts has increased. For example, zeolites are part of the catalyst system used by Mobil Oil Company to convert CO and H_2 to gasoline (79, 80). The exothermicity of the reaction and the presence of water create severe conditions for the traditionally sensitive zeolite materials (1). The recent developments of ultrastable zeolites discussed in Section II-B-1 are therefore important advances in inorganic chemistry that will have an effect on these upgrading processes. It also makes zeolites more generally applicable as support materials for other reactions. The high thermal stability of refractory materials such as carbides, nitrides, borides, and silicides also offers an opportunity to improve existing catalysts. The attraction of such improvements increases in view of the potential chemical stability of these compounds, as discussed below. Finally, in the section dealing with the impact of materials science on catalysis (Section III), a new group of materials was discussed which display extremely high thermal stability. They are formed by the highly exothermic reaction of transition metals on the right of the periodic table (Group VIII, in particular Pd and Pt) with metals on the left such as Ti, Zr, and Hf of Group IV (81). The exothermicity of the synthesis of these compounds ($\sim$100 kcal mol^{-1}) suggest strong bonds, and therefore stable structure. The application of these materials to highly exothermic reactions has not been reported to date, and offers a unique opportunity in the use of novel compositions for coal conversion catalysis.

2. CHEMICAL STABILITY

In coal conversion and the upgrading of coal liquids there are a number of poisons which may affect the chemical integrity of the catalyst. A number of these were reviewed in Section VI of Part 1. Of particular concern are sulfur, carbon, and oxygen.

Sulfur is a problem in all coal conversion processes. In liquefaction it is present at high concentration ($\sim$1%), and as noted elsewhere (1) this severely limits the type of materials that can be used as catalysts. In effect, other than certain oxides, only sulfides have been known to survive in the presence of such high sulfur activity. From thermodynamic calculations, however, there are indications that borides, silicides, and phosphides of the Group VIII transition metals may be able to resist such an environment as well (1). This presents some interesting possibilities for liquefaction, and even more so for other conversion processes. Thus, in contrast to liquefaction, the catalytic upgrading of gasification products is particularly sensitive to very small amounts of sulfur. This places severe constraints on gas cleanup, and adds to the cost of conversion. For methanation, for example, the sulfur tolerance of currently used catalysts is less than 1 ppb. Low temperature scrubbing is therefore necessary. Improvements of only one order of magnitude in the sulfur tolerance could have substantial effects on the economics. Therefore, the above mentioned potential sulfur resistance of transition metal borides, phosphides, and silicides offer an opportunity for sulfur tolerant catalysts.

Several other materials may also have an impact for low sulfur concentration systems. Thus, if the electronic properties of a particular element can be modified, it is likely to have an effect on the interaction of this element with sulfur as well. In the preceding section, several classes of materials that may fall into this category were discussed. Transition metal exchanged zeolites, for example, show that the metal has an electron deficiency which modifies many of its properties, and is likely to affect their sulfur tolerance. Homogeneous catalysts can also, in principle, be modified in terms of their electronic properties by appropriate choice of ligands. Similarly, alloying has a substantial effect in the electronic properties of the original metals, an effect that is likely to be particularly important in small clusters. This applies to multimetallic clusters in organometallic complexes as well. In the extreme case, of course, formation of very strong intermetallic compounds such as $ZrPt_3$ is likely to have a substantial impact on the sulfur tolerance - beyond the contribution of each element. However, such strong compound formation may also adversely affect the catalytic properties of the material. Only experimental work can determine the promise of these compounds to catalysis.

Oxygen represents another general problem in conversion and upgrading reactions, primarily because current catalyst regeneration technology uses controlled oxidation as a means of carbon removal. The stability of oxides of both metals and non-metals leads to the general conclusion that most materials will be unstable in oxygen at high temperatures. Kinetic limitations may prevent oxidation at lower temperatures and diffusion limitations may prevent bulk oxidation for many materials. Silicides offer an example of the latter. However, in general, one has to contend with an environment that is very reactive. One consequence that is particularly serious involves volatile oxides such as RuO_4 or OsO_4 (and to a lesser extent PtO_2). The use of BaO_2 to stabilize ruthenium was discussed earlier, and provides an excellent illustration of the application of inorganic chemistry to chemical stability problems in catalysis. Similar use of oxides to stabilize catalytic materials in oxidizing environments has an impact in aspects of catalytic phenomena other than catalyst loss. Catalyst sintering, which will be discussed in Section III, is an example of such phenomena.

In addition to deposition on the catalyst surface, carbon presents another problem to many coal conversion processes: carbide formation. This is particularly important in the case of methanation, where carbiding ranks, together with sintering and sulfur poisoning, as one of the most severe complications (82). An examination of the heat of formation of various compounds (1) shows that for most transition metals, only nitrides and oxides are more stable than carbides. Borides of Group IV, for example, are considerably less stable (1). However, as one proceeds to the right of the periodic table, carbide stability decreases markedly. Most of the Group VIII carbides, for example, are unstable in sulfiding and/or oxidizing environments. Group VIII silicides and phosphides, on the other hand, are stable (1), and the same is expected for borides. These compounds therefore do not only offer opportunities for sulfur tolerance, as discussed earlier, but also a possibility for resistance to carbide formation.

3. STRUCTURES AND COMPOSITIONS OF INTEREST

The brief discussion presented in Section II-B illustrates the wealth and magnitude of the structures and compositions that have been reported in the inorganic chemical literature. Only a small fraction of these materials have been tested for catalytic applications. Many novel compositions are likely to exhibit surface properties of interest to the catalytic conversion of coal. A few examples will be reviewed in this section.

One of the concepts that was emphasized in Part 1 dealt with the formation of multimetallic clusters. The dramatic changes that have been reported in activity and selectivity patterns of reactions upon cluster formation (e.g. Os-Cu and Ni-Cu work of Sinfelt (83)) have implications in all areas where metals are used as catalysts. In the context of the present study, this includes methanation, Fischer-Tropsch synthesis, and upgrading of coal liquids. However, it is not only limited to zero valent metals. The synthesis of complex oxides with clusters of transition metals, for example, opens an entirely new spectrum of materials that display properties which are intermediate between oxides and metals (11). This is particularly important for reactions which require activation of the hydrogen molecule in the presence of species such as CO which interact in many cases too strongly with zero valent metals to be effective catalytically.

Similarly, the presence of a metal cluster that maintains its metal-like integrity in an oxidizing environment (H_2O is present in water-gas shift, methanation, Fischer-Tropsch, and methanol synthesis) is likely to show interesting catalytic properties. When such a behavior is combined with the possibility of forming multimetallic clusters, advantage can be taken of the properties of the various components of the cluster. In the case of organometallic complexes discussed in Section II-B-5, this possibility has not yet been reported. However, it has been found that organometallic clusters exhibit catalytic behavior not found for the mono-metallic counterparts. Muetterties, for example, reports cyclization reactions in the presence of $Ni_4(CNC(CH_3)_3)_7$ which do not occur with $Ni(CNC(CH_3)_3)_4$ (63). In particular, acetylene is converted to benzene and butadiene to cyclo-octadienes (63). As pointed out by Norton (56), such cluster organometallic complexes may in fact be able to catalyze the reduction of CO by hydrogen, a reaction that has not been catalyzed by a mono-organometallic complex to date. The presence of a multimetallic system may aid in achieving the correct electronic balance for such a reaction.

As pointed out in Section II-B-2, complex oxides are not the only compounds that exhibit cluster formations with very close metal-metal distances. A number of other compounds, in particular sulfides, show a similar structure ($Al_{0.5}Mo_2S_4$, $PbMo_6S_8$, MoN, Mo_3Se_4 (1)). It is likely that in the future other sulfospinels which display similar characteristics will be synthesized. Stability in H_2S and the higher hydrogenation-dehydrogenation activity of such cluster forming compounds can have a significant impact on coal liquefaction and other HDS operations.

The common interest in materials such as multimetallic and organometallic clusters is motivated by an attempt to vary the properties of elements through modifications of their electronic properties, either through alloying or formation of organometallic complexes. Two other systems have been discussed for which such changes have been demonstrated: noble metal-exchanged zeolites and carbides such as WC. Pt-exchanged Y zeolites, for example, show much higher hydrogenation activity than expected for Pt (22). In effect, the activity is more characteristic of neighboring Ir. Electron withdrawal was subsequently confirmed by ESR (23). In the case of WC, it has been found that the carbide has an activity pattern that is very different from that of the parent metal (84). In effect, activity in the reduction of surface oxygen with H_2 and certain isomerization reactions is more characteristic of a noble metal than of tungsten. The electronic interpretation of this phenomenon is still a controversial subject (85).

Finally, another interesting family of compounds that have not been explored in catalysis should be mentioned: the Nowotny carbides and nitrides. They are complex compounds which contain two or more transition metals such as Pt_3ZnC. Several of the members of this class of compounds exhibit a structural similarity to the oxide perovskites mentioned in Section II-B-1. However, instead of the oxygen atom being the major component of the structural framework (such as in $BaRuO_3$), the Nowotny perovskites have a metal framework such as $ZnPt_3$ in Pt_3ZnC. The presence of interstitial carbon is likely to strengthen the compound without severely affecting the properties of the metals. Application of such compounds to upgrading of coal liquids and to reactions where carbiding is a problem (such as methanation) would be of interest.

D. CONCLUSIONS

Inorganic chemistry is central to a number of aspects of catalysis, in particular in the effort to discover new materials with improved catalytic properties. It affects all of the catalytic steps in coal conversion, as illustrated by the many new concepts and materials discussed above.

The catalytic chemist is faced with two challenges. First he has to choose among the literally thousands of compositions and structures available to him through the inorganic chemistry literature. Second he has to devise new methods for the synthesis of the materials in high enough surface areas to be attractive for catalytic applications.

For the first challenge, thermodynamics provides an initial guideline to the choice of materials that will withstand a particular environment. This has been discussed briefly in the above sections.

For the second challenge, many of the advances made over the last decade in the area of catalyst synthesis should provide some basic guidelines for the synthesis of new materials, as discussed in Part 1.

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