

NEW MATERIALS FOR COAL LIQUEFACTION

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INTRODUCTION

Direct liquefaction is one of the alternatives currently under development for the production of clean burning fuels from coal. In the more advanced liquefaction processes, such as those of Gulf Research and Development, Hydrocarbon Research, Inc., and the Bureau of Mines (synthoil), coal is liquefied in the presence of a cobalt-molybdate catalyst at moderate temperatures (400°C) and high hydrogen pressures (2000-4000 psi). Extensive research is currently underway (1) to improve the performance of these catalysts. Properties of importance include activity (to reduce reactor size and pressure) activity maintenance (to increase life and regenerability) and selectivity (to minimize hydrogen consumption). The catalyst performs a number of functions such as cracking large aromatic molecules present in coal liquids and hydrogenation of certain cracked molecules with concomitant removal of heteroatoms such as sulfur, nitrogen and oxygen.

Because of the projected need for clean-burning liquid fuels and the technological complexity of existing liquefaction technology, first generation processes are likely to be based on existing catalyst technology. However, it is clear that there is room for substantial improvements in all aspects of the process, improvements that will require new catalytic materials and concepts. It is therefore timely to establish some of the ground rules which will guide the catalytic scientist and engineer in the choice of new materials to be tested as catalysts for coal liquefaction. This was the objective of a study recently conducted for the Electric Power Research Institute (2) and summarized in this report.

In this summary, the general criteria for the selection of materials for coal liquefaction catalysis are discussed first. This serves as a basis for a detailed analysis of a number of compounds and a preliminary assessment of the types of compounds that should be tested for coal liquefaction.

CRITERIA FOR SELECTION OF MATERIALS

A discussion of new materials requires, in effect, a look at the enormous number of compounds that have been investigated in solid state and inorganic chemistry over the years. A number of the most important classes of compounds are shown in Table 1. They are formed by transition and alkaline earth metals and a small group of nonmetals from the upper right hand corner of the periodic table of the elements: boron, carbon, silicon, nitrogen, phosphorous, oxygen, sulfur and chlorine.

Considering the wealth of compounds represented by these various groups, it is interesting to note that relatively few have been tested for catalytic applications. Furthermore, it is difficult to choose a priori from this large number of materials those which would be applicable for study as liquefaction catalysts. The challenge in the selection sequence for new materials is therefore the identification of those constraints that have to be met by a compound in addition to its catalytic activity. Among the most important constraints for coal liquefaction are thermal and chemical stability.

Thermal stability takes into account the resistance of a given material to volatility, melting, sintering, and general mechanical failure. Temperatures which must be considered are both those for reaction and regeneration. The reaction temperatures for catalytic liquefaction processes are currently of the order of 400°C.

The regeneration scheme which is most likely to be applied to these process is controlled oxidation of the carbonaceous residues which are deposited on the surface of the catalyst. Although this is carried out with careful control of temperature, surface temperatures can frequently exceed 800°C. Continued use and regeneration brings about structural degradation of many materials at these conditions. Chemical stability relates to the chemical behavior of the materials in the environment of coal liquefaction and regeneration. Of primary concern in this respect is the stability of the catalyst in an H₂S/H₂ atmosphere. In coal liquefaction, concentrations of H₂S of 1-5 percent or higher are normal. Other reactive compounds that may affect stability are hydrocarbons, NH₃, H₂O, and O₂. Except for oxygen used in regeneration, the effect of the other reactants is minimal compared to that of H₂S.

In spite of the lack of catalytic information for many of the compounds shown in Table 1, the focus of a general survey such as the present one will be those materials containing cations that have shown catalytic activity. This is the reason for the emphasis on transition metals compounds. The thermal and chemical stability of these materials will now be discussed.

THERMAL STABILITY

The only compounds in Table 1 that are clearly excluded from further consideration because of poor thermal stability are the organometallic complexes. For example, Co₂(CO)₈ decompose to the metal at temperatures as low as 150°C, unless the CO pressure in the system is greater than 600 psi (3). By contrast, some of the compounds in Table 1 can withstand temperatures that are among the highest of any material. For example, TaC melts at about 3980°C (4) and TiB₂ melts at 2980°C (5). In spite of this high thermal stability, the chemistry of these compounds changes with temperature and the stable stoichiometry at the synthesis temperature may be quite different from that at the temperature of operation. This is illustrated quite dramatically by a compound that has been considered for hydrogenation and desulfurization, VS₄ (6). An examination of a simplified phase diagram for this material reveals that above 300 to 400°C VS₄ decomposes to sulfur and the next stable stoichiometry, V₅S₈ (7) (although there are indications that V₃S₅ may also be formed (8)). It is therefore unlikely that at operating conditions VS₄ is the actual catalyst.

A diagram of temperature vs. composition is not complete without a specification of pressure. In the case of the V-S system the pertinent parameter in the pressure of sulfur or, equivalently, a sulfur containing compound such as H₂S. The behavior of compounds in the presence of H₂S depends on the chemical stability of the compound and is discussed in the next section.

CHEMICAL STABILITY

The two conditions that are most critical in coal liquefaction are the high H₂S concentration and the need (unless alternate methods are discovered) to use oxygen to regenerate the spent catalyst. Before these two conditions are discussed, it is of interest to explore the behavior of compounds in the presence of the "parent" non-metallic element, namely the free energy of formation. For convenience, all the comparisons are made at 700K (which is comparable to current coal liquefaction temperature). Thermodynamic calculations are based on the latest published data and have been discussed in detail elsewhere (2). An extremely useful simplification, proposed by Searcy (9), allows direct use of heats of formation in the absence of values for the entropy change. This permits considerable extension of the published data and leads to some interesting conclusions concerning potential new materials for coal liquefaction catalysis.

Free Energy of Formation

By comparing free energies of formation it is possible to make a qualitative evaluation of the relative stability of various compounds. This in turn can be used to predict the behavior of these compounds in certain chemical environments.

The free energies of formation of a number of compounds were examined in detail (2). Representative examples are shown in Tables 2 and 3. The following general observations are of interest for the present study:

- a. Oxides are the most stable compounds of the groups that were examined. In effect, the following stability trends are observed:

oxides >> nitrides > carbides

oxides > sulfides

oxides >> borides, silicides, phosphides

One consequence of these trends is that most compounds are expected to be thermodynamically unstable in an oxidizing environment such as encountered in catalyst regeneration.

- b. In general, the stability of a family of compounds decreases with increasing group number in the periodic table. Group VIII oxides, for example, are the least stable of the transition metal oxides. However, the extent of this decrease is not the same for all groups of compounds. It is most severe for nitrides and carbides, least severe for silicides. In general, the following order of stability change is observed:

nitrides, carbides >> oxides > sulfides > silicides

This difference is manifested in the variation in stability of members of one group of compounds (such as oxides) in the presence of the same environment. In H₂S, for example, titanium oxide (Group IV) is stable. Cobalt oxide (Group VIII), on the other hand, is not.

- c. Thermodynamic information on borides is limited to the Group IV elements Ti, Zr and Hf. For these elements borides are more stable than silicides. From the similarity in many of the physicochemical properties of borides and silicides, it is expected that this behavior will continue throughout the periodic table. The behavior of silicides in H₂S can therefore be used as a guide to the stability of borides in this environment.

Stability in the Presence of H₂S

The high H₂S concentrations present during coal liquefaction imposes a most severe constraint on the choice of catalytic materials. Levels as high as 1-5% H₂S can be expected. From the thermodynamics of sulfide formation it is found that most materials are unlikely to survive in this environment (2). Thus, at any reasonable process conditions, metals, alloys, organometallic complexes, carbides, and many oxides and nitrides can form the respective sulfide. However, as indicated earlier, the behavior of individual transition metals depends on their position in the periodic table. Some representative examples are shown in Table 4. In general, the following is observed:

- a. While oxides and nitrides of Group IV are stable in H₂S, those of higher groups can form the sulfide.
- b. Conversely, while borides and silicides of Group IV are thermodynamically unstable in H₂S, those of group VIII are expected to survive even in severe H₂S environments.

- c. Many of the metals that are in the region of intermediate stability (Groups V, VI and VII) are likely to form complex compounds, such as oxysulfides, in the presence of H_2S . Formation of these compounds is a sensitive function of the H_2S pressure in the system.

It should be emphasized that the above statements are based on thermodynamic information only. No conclusions can be drawn concerning the kinetics of the respective transformations. However, the thermodynamic analysis does provide a guideline for the expected behavior of a system under the most adverse conditions.

CONCLUSIONS

Before a new material is tested for catalytic coal liquefaction, its chances of survival in the liquefaction environment should be examined. The presence of H_2S poses the most severe problem. A large number of compounds that may ordinarily be considered promising candidates sulfide in this environment. It is therefore fruitless to spend considerable effort in the testing of these materials. Compounds that are expected to resist sulfidation include a number of oxides, nitrides, borides and silicides. Among these there are a number of interesting compositions that have not been tested for catalytic liquefaction to-date. Examples are $Mg_2Mo_3O_8$, which has Mo_3 clusters and has been found to exhibit hydrogenation activity intermediate between metals and oxides (10), the perovskite-like Nowotny nitrides such as Ni_3AlN , and the borides of the group VIII metals such as CoB and NiB . Serious consideration, of course, should also be given to the large number of sulfides that have been synthesized and characterized over the last few years, (an example is $Al_{0.5}Mo_2S_4$, which also contains Mo_3 clusters (11)) and to sulfo-compounds such as oxysulfides which are likely to be formed by many of the compounds of intermediate stability. Some of these are being uncovered only recently, including Ta_2S_2C (12) which is capable of forming intercalation compounds and also retains the layered structure that is characteristic of a number of currently used hydrotreating catalyst.

If an alternative to oxidative regeneration is not found, even some of the sulfur resistant materials mentioned above will not be viable candidates for catalytic coal liquefaction unless they exhibit unusual activity maintenance and therefore require no or infrequent regeneration. It was observed earlier that a number of the compounds under consideration are likely to be thermodynamically unstable in an oxidizing environment. It is therefore important to consider how they will be resynthesized to the stoichiometry that is catalytically active. Sulfides, and oxysulfides, of course, present no problem. Carbides and even nitrides may be feasible. The use of PH_3 or B_2H_6 to resynthesize borides and phosphides is probably impractical. This further restricts the best candidates for catalytic liquefaction unless more economical reagents or means for resynthesis are developed. It should be mentioned that even among those classes of materials which may endure oxidative regeneration (e.g. carbides, nitrides, oxides, sulfides, oxysulfides and mixed systems) numerous compounds exist which are of interest for exploration as future generation liquefaction catalysts.

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TABLE 1
REPRESENTATIVE CLASSES OF COMPOUNDS

Oxides	Simple	Al_2O_3, MoO_3
	Complex	$Mg_2Mo_3O_8$
Sulfides	Simple	V_5S_8
	Complex	$Al_{0.5}Mo_2S_4$
Carbides	Simple	WC
	Complex	Pt_3SnC
Nitrides	Simple	Co_3N_2
	Complex	V_3Zn_2N
Borides	$MoB, Co_{21}Hf_2B_6$	
Phosphides	Co_2P	
Silicides	Mo_3Si	
Alloys and Inter-metallic Compounds	Ni-Cu, ZrPt ₃	
Organometallic	$Co_2(CO)_8$	
Molten Salts	$ZnCl_2$	
Solid Acids	Zeolites, Clays	
Solid Bases	$CaO, NaNH_2$	

TABLE 2
STANDARD FREE ENERGIES OF FORMATION ($-\Delta G_f^0$) OF
REPRESENTATIVE OXIDES, SULFIDES, CARBIDES, & NITRIDES
(In kcal/g-atom Non-Metal At 700 K)

	<u>Oxides</u>		<u>Sulfides</u>		<u>Carbides</u>		<u>Nitrides</u>	
Group IV	TiO	108	TiS	64	TiC	44	TiN	65
	TiO ₂	97	TiS ₂	39				
Group V	NbO	84	NbS ₂	47	NbC	34	NbN	42
	NbO ₂	79						
Group VI	MoO ₂	55	MoS ₂	33	MoC	3	Mo ₂ N	2
	MoO ₃	45						
Group VIII	CoO	42	Co ₉ S ₈	25	Co ₂ C	-4	Co ₃ N (unstable)	
			CoS ₂	19				

TABLE 3

STANDARD FREE ENERGIES OF FORMATION ($-\Delta G_5^0$) OF
 REPRESENTATIVE BORIDES, SILICIDES, & PHOSPHIDES
 (In kcal/g-atom Non-Metal At 700 K)

	<u>Borides</u>	<u>Silicides</u>	<u>Phosphides</u>
Group IV	TiB 39 TiB ₂ 22	TiSi 31 TiSi ₂ 16	a
Group V	a	NbSi ₂ 16	a
Group VI	a	MoSi 14	a
Group VIII	a	CoSi 19	CoP 29

a. Data unavailable

TABLE 4

EXAMPLES OF STABILITY IN THE PRESENCE OF H₂S

	<u>Reaction</u>	<u>$\Delta G^0_{700 K}$</u> ^a
Oxides:		
Group IVB	TiO ₂ → TiS	+22
Group VIB	MoO ₃ → MoS ₂	-33
Nitrides:		
Group IVB	TiN → TiS	+22
Group VB	TaN → TaS ₂	- 7
Group VIB	Unstable Nitrides	<< 0
Silicides:		
Group IVB	TiSi → TiS	-18
Group VIIB	MnSi → MnS	-12
Group VIIIB	NiSi → NiS	+12

a. Free energy of sulfide formation at 700 K in kcal/g-atom non-metal. Negative free energy indicates a favored reaction.