

V. CONVERSION OF SRC TO LOW SULFUR,  
LOW NITROGEN LIQUID BOILER FUELS

A. INTRODUCTION

In solvent refined coal (SRC) most of the inorganic sulfur and mineral matter are removed by dissolution of coal in an aromatic solvent (e.g. anthracene oil) and subsequent filtration of the liquid. Typical conditions for dissolution are 800°F and a hydrogen pressure of 1000 psi. After filtration the solvent is recovered by evaporation and recycled. The product is a coal with a low melting point (approximately 350°F) and relatively low sulfur and mineral levels, as shown in Table V-1.

The purpose of the present section is to explore the research and development programs that are required to upgrade SRC to a liquid boiler fuel. The requirements for boiler fuel are typically a hydrogen to carbon ratio of 1.6 and nitrogen, sulfur, and mineral levels below 0.5 wt.%. The sulfur level is determined by environmentally acceptable SO<sub>2</sub> emissions. The current EPA standard is 1.2 lb. SO<sub>2</sub>/MMBTU. This is equivalent to a sulfur concentration in SRC of 0.96 wt.%:

$$\frac{16000 \text{ BTU}}{1 \text{ b SRC}} \times \frac{1.2 \text{ lb SO}_2}{10^6 \text{ BTU}} \times \frac{1 \text{ lb S}}{2 \text{ lb SO}_2} = 0.96 \times 10^{-2} \frac{\text{lb S}}{1 \text{ b SRC}}$$

If the SRC process can reduce sulfur below this level, and all estimates indicate that it can, then the major steps required for the conversion of SRC to a liquid boiler fuel are:

- a. A reduction in the nitrogen levels to less than 0.5 wt.%, and
- b. An increase in the hydrogen content of the fuel.

TABLE V-1  
TYPICAL ANALYSIS OF COAL SAMPLES<sup>1</sup>  
(WEIGHT PERCENT)

	<u>Coal</u>	<u>SRC</u>
Carbon	70.75	88.4
Hydrogen	4.69	5.2
Nitrogen	1.07	1.8
Sulfur	3.38	0.8
Oxygen	10.28	3.7
Ash	7.13	0.1
H/C Atom Ratio	0.80	0.71
Heating Value (BTU/lb)	12,821	16,000

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<sup>1</sup> Analysis by Pittsburgh and Midway Coal Company, data from "Synthetic Fuels Data Handbook", Cameron Engineers, Inc., Denver, Colorado, 1975, p. 224.

The present analysis will therefore concentrate on these two basic requirements. However, some emphasis will be placed on HDS as well since EPA standards on sulfur emissions are likely to become more stringent in the future.

In this section, a brief summary of the constraints and problems involved in upgrading SRC will be presented first, followed by an analysis of the new developments and concepts discussed in Parts 1 and 2, which may impact on these problems.

## B. CATALYST CONSTRAINTS AND PROCESS REQUIREMENTS FOR SRC UPGRADING

Recent work by Mobil (1) has shown that SRC contains a high fraction of asphaltenes, and has the highest aromatic content of a number of coal liquids tested. The problems that this may present to the activity, selectivity and activity maintenance of SRC will be discussed in this section.

### 1. ACTIVITY

In the hydrotreatment of petroleum residuum, one of the main problems with catalyst activity is a fast initial deactivation due to the deposition of carbonaceous materials (2). This is accompanied by the deposition of mineral matter, which continues throughout the reaction. The relationship between the structure of residuum and this initial carbon deposition is not clear. It is believed to be due to the large asphaltene molecules present in residuum (3). The average size of these molecules, 40 to 50 Å, is in the range of the size of the micropores in conventional alumina catalyst supports. This therefore leads to plugging of small pores which represent a large fraction of the total catalyst surface area.

Optimization of the pore size distribution is therefore necessary. In SRC, the carbon deposition problem is likely to be at least as severe as observed for petroleum processing due to the high asphaltenic content of the coal. Similarly, the minerals in SRC are expected to present a problem. The analysis of the SRC samples used by Mobil, for example, show high Fe (140 ppm), Ti (130 ppm) and Na (100 ppm) levels (1). These values are as high as the V and Ni levels found in certain heavy crudes. Total mineral content can be as high as 0.1%. This is still a large amount of ash. For example, a pilot plant processing 100 tons of SRC per day would handle up to 200 pounds/day of ash. This could have a considerable degradation effect on the catalyst.

In addition to the size factor, the acidity of the catalyst surface is likely to influence the rate of carbon deposition. Acidity is also an important parameter for the selectivity of hydrotreatment catalysts, and will therefore be discussed in the next section.

The presence of large molecules causes an additional problem in coal and residuum hydrotreatment processes, namely pore diffusion limitations. Furthermore, the presence of three phases leads to diffusion limitations in the main fluid stream. The choice of reactor systems used in catalyst testing is therefore particularly important for SRC as well as for other coal conversion studies.

## 2. SELECTIVITY

In terms of selectivity, the objective in coal conversion is to minimize the hydrogen consumption and to maximize a specific desired product slate. In the particular case of SRC upgrading to boiler fuels, the former is of primary importance. Product distribution is not a major constraint for

this application. As indicated earlier, hydrogen is necessary to decrease the viscosity of the fuel and to remove the nitrogen constituent of SRC. The acidity of the surface plays an important role in both of these steps. Thus, center ring cracking of the heterocyclic molecules should be maximized since it is the most effective mechanism to remove sulfur and nitrogen. The mechanism of cracking, however, is complex (4), and includes the participation of the acidic support as well as the catalyst. Both surface acidity and the nature of the catalyst are therefore important parameters in efforts to maximize selectivity. Most currently used liquefaction catalysts are designed for optimum HDS. This is not necessarily the best catalyst for SRC upgrading. Therefore, a considerable effort to optimize selectivity will be required in an SRC upgrading program.

### 3. ACTIVITY MAINTENANCE

In spite of the efforts to minimize HDS, some sulfur removal is likely to occur during SRC upgrading. The presence of  $H_2S$  will therefore have to be included in catalyst stability considerations. It places a constraint on the choice of catalyst materials, limiting it to compounds that are compatible with an  $H_2S$  environment. The constraint will not be as severe, however, as the one encountered in other direct liquefaction processes, where  $H_2S$  levels can be 1-5%.

In addition to the chemical stability problem in the presence of  $H_2S$ , the regeneration of coal conversion catalysts creates some serious thermal stability limitations. Sintering of both catalyst and support may occur. Both vanadium and sodium are believed to lead to irreversible surface area loss during regeneration of residuum hydrotreating catalysts (5). While vanadium is not found in SRC, the presence of sodium may cause similar problems.

### C. IMPORTANT RESEARCH DEVELOPMENTS

In Section VI of Part 3, the catalytic hydrocracking of coal or lignite to low sulfur, low nitrogen liquid boiler fuels will be discussed. Both HDS and HDN are important in that case. In this section, the main emphasis is the reduction of the nitrogen content of SRC and an increase in the hydrogen to carbon ratio of the coal. It is useful to divide the pertinent developments and advances presented in Parts 1 and 2 into short and long term, depending upon the complexity of the development and its applicability to existing or future technology. In addition to these two aspects of the problem, it is important to summarize a number of developments directed towards a better understanding of upgrading reactions and which provide a foundation for new science and technology in this area. They will be presented at the end of this section.

#### 1. SHORT TERM DEVELOPMENTS

The discussion of the constraints and problems expected for SRC upgrading was divided into three aspects of the problem: activity, selectivity, and activity maintenance. It is effective to discuss activity and selectivity together since many of the developments presented in Parts 1 and 2 are pertinent to both of these areas.

Before proceeding with this discussion, it is useful to consider some of the factors which determine whether SRC upgrading could be competitive with alternative processes such as the direct liquefaction of coal to boiler fuels. In making this comparison, it is important to consider the unique composition of SRC and its effect on catalyst performance during the upgrading operation. In this respect, there are three important properties of SRC: low mineral content, chemical structure, and relatively low sulfur and high nitrogen concentrations. The effect of these properties on catalyst activity, activity maintenance, and regeneration will

have to be investigated in any short term R & D effort in this area. It will be necessary, for example, to determine whether the mineral content of SRC is sufficiently low to minimize catalyst attrition as well as catalyst deactivation due to deposition of mineral matter on the coal. Similarly, it will be important to consider the chemical structure and composition of SRC, since it will determine carbon deposition on the catalyst, and therefore catalyst deactivation. Finally, it should be assessed whether the low sulfur composition of SRC would permit the use of more effective HDN catalysts than currently used in other coal liquefaction processes.

Unless these properties of SRC facilitate upgrading to boiler fuels considerably compared to direct liquefaction, the additional processing may not be warranted. A number of advances discussed in Parts 1 and 2 which are pertinent to this question will be presented in the next sections.

a. Activity and Selectivity

As already indicated, hydrotreating is believed to require a multifunctional catalyst (4). The use of multifunctional systems in chemical processing is not new. In catalytic reforming of naphtha, for example, a dual functional catalyst has been used since the 1950's (6). The success and improvement of reforming catalysts is in large measure due to the existence of techniques for catalyst characterization which allows determination of the specific surface area of the various catalyst functions. Elucidation of their respective roles and comparison between different catalysts is therefore facilitated considerably.

While characterization procedures for metallic catalysts used in reforming are now well established and used routinely (7), this is not the

case for the oxide catalysts used for coal conversion. Characterization of supported non-metallic catalysts is more complex (8), and has not received nearly as much attention. However, in the last few years there have been a number of promising developments in this area (7). Of particular interest to SRC upgrading is the use of NO chemisorption for the determination of the specific surface area of oxides. Systems that have been studied with this technique include the oxides of Fe, Co, Ni, Cu, and Cr supported on  $Al_2O_3$ . The technique should be applicable to other oxides as well. Similar efforts to study the adsorption properties of other gases on various supported oxides have not been extensive. A recent report does suggest that  $H_2S$  can, in fact, be used to obtain an estimate of the active sites on a  $CoO-MoO_3-\gamma-Al_2O_3$  catalyst (9). This type of adsorption work is going to be important in the efforts to improve currently used HDN and liquefaction catalysts.

As discussed earlier, one of the problems of hydrotreating catalysts is carbon deposition at the initial part of a test run, leading to rapid deactivation. It was suggested that control of the pore size distribution can reduce the severity of this deactivation. The extent of deactivation depends on the feedstock and the conditions of reaction. For this purpose, the optimum pore size distribution for SRC upgrading should be determined. It is likely to differ from that used for HDS since conventional HDN technology, in general, requires more severe reaction conditions (4). New developments in the preparation of support materials of controlled surface area, pore volume, and pore size distribution are of particular interest. For example, gel procedures using an organic gelling agent have been used successfully in the preparation of oxides and mixed oxides with variable physical properties (10). Similarly, the nuclear industry has



placed a considerable effort in the preparation of mixed oxides with controlled physical properties (10). Many of these developments are likely to be useful in the preparation of catalytic supports and the optimization of properties such as pore volume and pore size distribution.

One parameter that has to be included in efforts to optimize pore size distribution is the mechanical strength of the catalyst. In general, an increase in the pore size leads to a decrease in crush strength. There are indications that the addition of certain alkaline and rare earth cations improve the strength of catalyst supports (11). This possibility should be explored in more detail.

As indicated above, the effect of pore plugging due to carbonaceous materials can be reduced by changing the pore structure of the catalyst. Another variable that affects carbon deposition is the acidity of the support. Tests of catalyst performance as a function of surface acidity are important for the optimization of the activity as well as the selectivity of the catalyst. Many methods for acidity measurement have been developed in the last decade, and are now routinely used (12). They include the measurement of acid strength, amount, type, and distribution. Paralleling the advent of these measurement techniques, considerable progress has been made in the synthesis of mixed oxides displaying a wide range of surface acidity properties (10). They will contribute significantly to the improvement of coal conversion catalysts, both in terms of activity maintenance (minimizing coking) as well as selectivity (minimum  $H_2$  consumption). In addition to minimizing carbon deposition which is a problem that is common to all coal conversion processes, optimization of SRC upgrading catalysts will require significant improvement in the hydrodenitrogenation

activity. Mechanistic studies suggest that cracking of the carbon-nitrogen bond of a heterocyclic molecule is the rate determining step for the HDN reactions at the conditions usually used for this process (13). In the commonly used cobalt molybdate system, there are indications that Mo is responsible for the cracking activity (14). Therefore, an increase in the strength of the Mo-N interaction is likely to have a significant effect on the HDN activity. Similar arguments hold for Co-W, Ni-W, and Ni-Mo catalysts. Over the last decade, a number of studies have shown the possibility of changing the properties of a catalyst through the chemical interaction of the catalyst with the support (15). This effect is likely to be most pronounced for supported oxide catalysts. Interaction of molybdenum oxide with an appropriate support may be one method to vary the strength of the Mo-N interaction and thus influence HDN activity (16). Other methods, including the application of new materials such as complex oxides and oxysulfides, are discussed in the next section.

In terms of short term developments, improvement efforts should concentrate on modifications of currently used hydrotreating catalysts to optimize catalyst morphology and composition for HDN and SRC liquefaction. The need for modification is most clearly seen in the effect of the Co-Mo ratio on HDN activity. For example, the conversion of pyridine is similar for  $\text{CoO-MoO}_3/\text{Al}_2\text{O}_3$  and  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalysts (14). This result suggests that, in contrast to HDS, the presence of Co is not important for HDN. Optimization of currently used liquefaction catalysts is therefore a necessary step for their effective use in SRC conversion. Finally, it should be noted that catalyst preparation and pretreatment procedures can have a profound effect on the performance of the catalyst. These effects need to be taken into account in any catalyst R & D program.

## b. Activity Maintenance

The use of catalyst-support interactions to stabilize a catalytic system is being reported in an increasing number of areas of catalysis (17). It is particularly important in high temperature processes such as auto exhaust emissions control and catalytic combustion. While it has been applied primarily to metallic catalysts (such as Pt and Pd used in automotive exhaust oxidation and Ru used in NO<sub>x</sub> reduction), it is likely to be especially effective for non-metallic supported catalytic systems (17). This is due to the large interaction that is expected to occur between a non-metallic catalyst and the non-metallic support. The constituents of the support are therefore chosen in such a way that they optimize the catalyst support interactions. The choice is made on the basis of the solid state chemistry of the catalytic material. Molybdenum, for example, is known to interact with alkaline earth oxides to form complex oxides such as Mg<sub>2</sub>Mo<sub>3</sub>O<sub>8</sub> (18). A surface interaction of the molybdenum compound with such an alkaline earth oxide may thus offer an interesting method of stabilization. Interaction of the alkaline earth oxide with the support completes the system.

Thermal stabilization of the support is another area of importance in the improvement of existing hydrotreatment catalysts. Recent patents show that cationic doping prevents the high temperature transformation of Al<sub>2</sub>O<sub>3</sub> to the low surface area  $\alpha$ -form (11). These materials have found use in high temperature applications such as catalytic combustion and automotive exhaust control. They are expected to improve the behavior of HDN and liquefaction catalysts, in particular during oxidative regeneration.

The addition of dopants to a support and the formulation of a support to optimize catalyst-support interactions should take into account

the sulfiding tendency of the components of the catalyst system. As discussed earlier, the SRC conversion catalyst will be placed in an H<sub>2</sub>S environment in spite of the fact that HDS is not its main function. The sulfiding tendency of many oxides and elements is very sensitive to the H<sub>2</sub>S pressure (19), and therefore the steady state behavior of the SRC catalyst may be different from that encountered in other systems. This behavior has to be determined in an improvement program. Some aspects of this H<sub>2</sub>S sensitivity which require a longer range commitment are discussed in the next section.

## 2. LONG TERM DEVELOPMENTS

The application of many of the advances and developments discussed in Parts I and 2 to the specific problems of SRC upgrading may require a more extensive R & D program than expected for the short term developments discussed in the prior section. They include the application of new synthesis methods and the development of new catalytic materials. These two areas are discussed separately in this section.

### a. New Synthesis Methods

In the prior section it was stressed that the preparation of catalytic materials with controlled physical properties such as pore size distribution and chemical properties such as surface acidity are important aspects for the development of effective SRC conversion catalysts. Many of the long term developments considered here are an extension of the novel preparative procedures discussed earlier.

In terms of controlled acidity, a considerable amount of work has been done in the last decade to study and tabulate the variation in acidic properties of mixed oxides with composition (20). Combining this understanding of mixed oxide acidity with new techniques for the preparation of high surface area mixed oxides (10) is likely to lead to new

catalytic materials of interest for the conversion of coal. One procedure of special interest, the so-called "Aerogel" technique, has been used to synthesize mixed oxides such as  $\text{NiO}\cdot\text{Al}_2\text{O}_3$  and  $\text{NiO}\cdot\text{MoO}_2$  with surface areas as high as  $600\text{ m}^2\text{g}^{-1}$ . These high surface area oxides may well provide the basis for the preparation of a number of new complex oxides which in the past could not be tested due to low surface area.

A number of other gel procedures have been described in the patent and scientific literature. In one of these, the formulation incorporates several oxides including a molecular sieve (21). The zeolite showed remarkable thermal stability, and the oxide system is reported to have unprecedented activity and activity maintenance for HDN of heavy feedstocks. The key to this formulation is the high stability of the zeolite component and the uniform and homogeneous nature of the catalyst.

A number of other ultrastable zeolites have been reported recently (22). Thermal stability in these zeolites is achieved by treatment procedures which are believed to remove some of the tetrahedrally coordinated aluminum. The samples withstand temperatures as high as  $1000^\circ\text{C}$ , and are very stable even at higher temperatures in the presence of water. It should be noted that the cracking and isomerization properties of zeolites are of great interest for the liquefaction of coal. However, stability problems made zeolites impractical in the past, and therefore the preparation of ultrastable zeolites is an important advance towards the application of these materials to coal conversion.

b. New Materials

As discussed in Section II of Part 2, and in more detail elsewhere (23), one of the major factors which limits the choice of new catalysts for direct coal liquefaction is the presence of  $\text{H}_2\text{S}$ . The choice

of possible catalytic materials increases considerably as the  $H_2S$  concentration in the reaction medium is lowered. In SRC upgrading there is a unique opportunity to optimize this condition since, as indicated in the introduction, only a minimal amount of HDS is necessary to produce an acceptable boiler fuel. Some limitations, however, cannot be avoided. For example, it is expected that metals and most alloys will sulfide since it is unlikely that the  $H_2S$  concentration can be reduced below levels of the order of 0.1% which are required to avoid bulk sulfidation (see Table II-3, Part 2). However, if the catalyst is formulated to minimize HDS, the  $H_2S$  concentration can be kept at a minimum, and a number of interesting new materials can be tested for HDN and hydrogenation. The possibilities are numerous. Possible candidate materials include transition metal borides (24), a number of promising carbides including the so-called Novotny phases which exhibit interesting structures containing several metal atoms (25), boride-carbides such as  $Mo_2BC$  (24), cluster compounds such as  $Co_2Mo_3O_8$  (26) and  $Al_{0.5}Mo_2S_4$  (27), and a large number of interesting nitrides which should be explored for HDN (25). Among the latter there are a number of complex nitrides which are similar to the Novotny carbides and have not before been tested for catalytic applications.

In the efforts to develop improved HDN catalysts, it will be important to continue experimental work designed to increase the understanding of this process. As discussed in detail in Part 1 (13), the current belief is that the rate determining process is the cracking of the nitrogen-carbon bond. Therefore, an increase in the nitrogen-catalyst interaction will be important in efforts to improve HDN activity. Variations in the composition of some of the complex oxides, oxysulfides, and other compounds discussed above are likely to lead to an optimization of

this property.

In the efforts to identify new and improved catalysts, testing for HDN activity should be conducted with real feeds rather than only with model compounds. A study of the hydrodenitrogenation of shale oil, for example, suggests that there is considerable interaction between the various nitrogen compounds that are expected to be present in shale, residuum, and coal (28). Relative activities for one constituent may therefore not hold in the presence of a mixture of heteroatoms. Similarly, the presence of  $H_2S$  is an important factor in the HDN activity of conventional catalysts, and its effect should be tested for other catalysts as well.

### 3. SUPPORTING RESEARCH

It is clear from the above discussion that the equilibrium of  $H_2S$  with the catalytic material is an important factor in the development of new coal conversion catalysts. As discussed in Section II of Part 2, only limited information is available for sulfide formation for most materials. It is particularly important to have a knowledge of the thermodynamics in the presence of variable amounts of  $H_2S$ . The stoichiometry of a sulfide is very sensitive to sulfur pressure (29). Stoichiometries therefore change significantly at different conditions, and this is likely to affect the catalytic behavior of the compound. Knowledge of the thermodynamics of sulfide formation is therefore crucial in the choice of potential new catalysts. Studies in this area should include the possibility of partial sulfidation of a number of compounds. This is particularly important for oxide systems, since oxysulfides are likely to be part of the deactivation-regeneration cycle of any conversion system using oxidative regeneration.

Another area of interest for the general understanding of coal conversion processes is the effect of particle size on the reactions. It has been shown to be an important aspect of the hydrogenation activity of  $WS_2$  catalysts (30), and may well be significant for HDN. The effect has not been investigated for other systems, primarily because of the difficulties in catalyst characterization discussed earlier. However, an understanding of this phenomenon is likely to be particularly important for the elucidation of the mechanism of HDN and liquefaction, and a better understanding of the role of the various components in the catalyst system (31).

The effect of particle size is related to the changes in structure and chemistry of the catalyst surface with size. A number of spectroscopic techniques have been studied in the last decade for the characterization of the surface of systems of interest in catalysis (32). However, as discussed in Part 2, these techniques will require considerable development before they can be applied routinely to most catalytic materials. Among the many new spectroscopies, a few exhibit unique capabilities which warrant further examination. Some of these capabilities have been applied to systems of interest to SRC upgrading and coal conversion. Measurement of surface composition of Ni-S catalysts by Auger electron spectroscopy, for example, has shown a relationship between composition and hydrogenation activity (33). This type of relationship is likely to be important in catalytic systems exposed to  $H_2S$ , such as encountered in SRC upgrading. Information on the surface composition-activity relationship together with a knowledge of the thermodynamics of the systems will be valuable in the development of optimum catalysts. Some techniques explore the chemical and electronic environment of the elements in the catalyst in addition to determining surface composition. In this context, ultraviolet photoelectron



spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS) have been used to determine the surface chemical state of a number of compounds including oxides and sulfides of Mo and Co (34, 35). This application of these techniques promises to provide a useful guide for understanding the surface properties of materials of catalytic interest before and after reaction. However, they cannot be used under reaction conditions. In this respect, a technique of great interest is x-ray adsorption fine structure spectroscopy (EXAFS) (36). It can in principle monitor the catalyst operation even in the presence of oil and coal.

Finally, a number of ion techniques have been studied in the last few years which have already demonstrated their applicability to catalytic systems (37). They are truly surface techniques, since they rely on collisions of ions with the surface to determine surface properties. Furthermore, they can in principle detect the presence of hydrogen, which cannot be detected by other spectroscopic methods. The latter is particularly important in the identification of the nature of carbonaceous materials that lead to the deactivation of coal conversion catalysts.

#### D. SUMMARY AND CONCLUSIONS

A wealth of concepts and developments are directly applicable to the upgrading of solvent refined coal. One of the keys to their application is the search for a catalyst that will selectively decrease the nitrogen content of SRC while upgrading it to a boiler fuel. By minimizing hydrodesulfurization, it is likely to lead to a less reactive environment (lower  $H_2S$  levels) than that encountered in direct liquefaction of coal, and thereby increase the choice of catalysts that may be active for this system. There is no reported precedent for a catalyst that will remove

nitrogen without removing sulfur. This is therefore a long term research goal. However, it is clear that even for conventional catalysts the optimum catalyst composition for HDN differs from that which is most effective for HDS. In the short term, the effort should therefore be directed towards optimizing currently used catalysts and maximizing nitrogen removal activity. Some sulfur removal, which will probably occur regardless of the system, will certainly also be useful in view of the likelihood for more stringent sulfur emission regulations.

The effort to improve the HDN activity of currently used catalysts will have implications that extend beyond SRC upgrading. In addition to the longer range effort of testing new materials, emphasis should be placed on the judicious choice of support constituents to optimize HDN activity by means of catalyst-support interactions. The latter is also important in efforts to stabilize the catalyst surface area, in particular during regeneration.

In terms of new materials, a number of new compounds and synthesis procedures developed in the last decade should be tested. Lower  $H_2S$  concentrations extend the choice of potential materials. A number of complex oxides, borides, carbides, and nitrides are interesting candidates. New synthesis methods may make it possible to prepare some of these materials in the high surface areas needed for catalytic applications.

Any effort to improve SRC upgrading catalysts will require the specific surface area of the catalyst. As for other areas of coal liquefaction, this is one of the important short term needs of the SRC upgrading program. It will allow identification of the role of the various components of the system, and lead to more reliable control of catalyst performance and deactivation. At the same time it will permit more accurate comparison of different catalyst preparations and formulations, and provide a basis

for assessing the effectiveness of regeneration procedures. The latter is a necessary part of any R & D program in this area.

Of equal importance is the identification of the role of pore size distribution (PSD) and surface acidity on the catalyst activity. This work should be directed specifically to SRC, since the composition of the liquids is the determining parameter for the optimization of these properties of the catalyst. A number of procedures for the variation of PSD and surface acidity which have been developed over the last decade will be applicable to this optimization effort.

Finally, parallel to these developments an effort should be mounted to provide needed supporting information, including a better understanding of the mechanisms of reaction, in particular HDN; an understanding of the effect of catalyst morphology, particle size, and composition; and a better knowledge of the thermodynamics of the compounds of interest in the presence of the type of environment expected during SRC upgrading.

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## VI. CATALYTIC HYDROCRACKING OF COAL OR LIGNITE TO LOW SULFUR, LOW NITROGEN LIQUID BOILER FUELS

### A. INTRODUCTION

The objective of coal liquefaction to boiler fuels is to increase the hydrogen to carbon ratio of the coal to that for a boiler fuel and to reduce the concentrations of sulfur, nitrogen, and mineral matter. A typical fuel oil has a H to C atomic ratio of the order of 1.6, and O, S, N, and mineral impurities which are each below 0.5 percent. The composition of coal, on the other hand, varies considerably with rank, and therefore liquefaction requirements vary accordingly. As shown in Table VI-1, bituminous coal has the highest sulfur concentration of the common coals, and lignite has the highest mineral content. Both sub-bituminous coal and lignite have high oxygen concentrations, and all three coals have similar nitrogen content and H to C atomic ratios.

Increasing the hydrogen to carbon ratio and decreasing the sulfur, nitrogen, and mineral content of coal requires a considerable amount of costly hydrogen. Therefore, minimization of hydrogen consumption is a primary requirement for any catalytic liquefaction process. To do this most effectively, it is necessary to carry out only that amount of hydrocracking which is required to remove the heterocyclic sulfur and nitrogen. This cracking should be primarily of the "center-ring" type to maximize liquid yields and minimize the formation of light gases. The process is complex, and there are a number of problems and constraints that have to be considered in any effort to improve catalyst performance. In the present section, these constraints are summarized and advances in catalysis

TABLE VI-1  
TYPICAL COMPOSITIONS OF COAL  
(WEIGHT PERCENT)

	<u>C</u>	<u>H</u>	<u>O</u>	<u>S</u>	<u>N</u>	<u>Other</u>	<u>H/C Atom Ratio</u>
Bituminous	73	5	9	3	1.5	8.5	0.82
Subbituminous	71	5	16	0.5	1.5	6.0	0.85
Lignite	64	4.6	18	0.5	1.5	11.4	0.86

and related disciplines which impact on the problems of liquefaction to boiler fuels are identified. Impacting advances are categorized according to their role in both short and long term development programs. In addition, a brief section on supporting studies of interest is included.

#### B. SUMMARY OF MAJOR CONSTRAINTS AND OBJECTIVES

Presently, two general approaches to direct catalytic coal liquefaction are being considered. One uses a heterogeneous catalyst, namely cobalt oxide and molybdenum oxide supported on alumina. The catalyst is run either in a fixed bed (e.g. the Synthoil process) or fluidized in an ebulliating bed, as practiced in the H-Coal process. In the fixed bed systems, coal liquids are contacted with the catalyst either in the presence of coal or in a separate reactor with a hydrogen-donor solvent. The donor solvent is usually hydrogenated and recycled. This type of process is similar to that being developed by Exxon.

The second general approach to liquefaction uses a metal halide melt as the catalyst. The melt, most commonly  $ZnCl_2$  (Consol process), provides improved catalyst-coal contacting and operates at a lower temperature and pressure than the cobalt molybdate system. However, it presently has several major limitations, including high catalyst-coal ratios (up to a factor of 3), catalyst deactivation due to reaction with sulfur, nitrogen, ash, and carbonaceous residues, stringent economic regeneration requirements, and the corrosive nature of the melt.

Catalyst improvements in the above mentioned liquefaction processes must overcome a number of constraints. These include:

1. Catalyst deactivation due to carbon deposition (which is most severe in the initial stages of the liquefaction), metals



deposition, and the interaction of other minerals with the catalyst or the support.

2. Catalyst poisoning by basic nitrogen and sulfur compounds.
3. Catalyst deactivation by sulfidation due to the high H<sub>2</sub>S concentrations encountered in all liquefaction processes.

This places a stringent thermodynamic constraint on the choice of catalytic materials. The severity of the environment varies with different coals, as expected from the figures shown in Table VI-1.

4. Effectiveness of the catalyst-coal liquid-hydrogen contacting and the diffusion limitations which are likely to occur in such a three phase system.
5. High hydrogen consumption and decreased liquid yields due to non-selective cracking.
6. Catalyst and support sintering, in particular during regeneration.
7. Poor heat and mass transfer properties because of improper control of pore size distribution.
8. Mechanical degradation with continued use and regeneration.

In the following discussion, the most important research developments that impact on these and other constraints of catalytic coal liquefaction will be highlighted.

#### C. IMPACTING AREAS AND RECENT RESEARCH DEVELOPMENTS

Some of the developments discussed in Parts 1 and 2 of this study have direct applicability to the problems faced by existing technology. Others offer solutions which require a more extensive R & D effort. For

convenience, the short and long term developments will be treated separately in this section. Furthermore, as discussed in the introduction, developments which impact primarily on the understanding of the nature of liquefaction process are summarized in a section on supporting research.

#### 1. SHORT TERM DEVELOPMENTS

It is convenient to focus the discussion of short term developments in terms of two aspects of catalytic liquefaction, one dealing with the activity and selectivity of the catalyst and the other with catalyst stability.

##### a. Activity and Selectivity

One of the major obstacles in the evaluation of the activity of existing liquefaction catalysts is the lack of catalyst characterization. To date, catalyst activity data in this area has been analyzed only on the basis of the total catalyst weight or surface area. The latter includes the surface area of the support, and is not necessarily proportional to the total active catalytic surface. Therefore, such information can often be misleading. Unfortunately, the question of specific surface area of non-metallic catalysts is complex, and few reliable and simple techniques exist (1). In recent years, however, a number of interesting leads have been uncovered, which may provide a basis for the development of routine techniques for the measurement of nonmetallic surface areas. They include the use of gases such as NO for the characterization of a number of oxides (1) and the use of room temperature H<sub>2</sub>S and H<sub>2</sub> adsorption for the characterization of Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts (2, 3). Further development of such techniques is central to considerations of the improvement of the activity of existing HDS and liquefaction catalysts.

Closely related to the problem of specific surface area determination is the need to identify changes in catalyst surface and bulk properties during the various stages of reaction. In many instances this is important because it is paramount to stabilize the surface or bulk compositions as well as the surface area of the active species. Catalyst-support interaction is a technique which was described in Part 1 (4) and which can have a significant effect on the final surface area or chemical state of the bulk surface of the catalyst. This is especially important for oxide catalysts on oxide supports, and a number of examples of such effects have been investigated over the last few years (4). The inorganic chemistry of compounds of interest such as cobalt and molybdenum oxides or oxysulfides with other metals may lead to suggestions of modifications of the support designed to maximize and maintain the active surface area. The formation of complex oxides such as the transition metal-alkaline earth metal oxides are of particular interest in this context (5).

In addition to the development of the concept of catalyst-support interactions over the last few years, considerable progress has been made in understanding the role of the support in catalysis. For example, the acidic properties of the support are important for determining the activity and selectivity of HDS and HDN catalysts (6). Recent developments concerning the control of these acidic properties by the preparation of mixed oxides and the variations of oxide composition (6) offer the opportunity to optimize this property for a given catalytic process. This may be especially important for HDN, where there are indications that rupture of the N-C bond is rate limiting. Therefore, the strength of interaction of the basic N atom with the surface may ultimately determine steady-state catalyst activity (7).

The deposition of metals and minerals on the catalyst surface is another problem related to overall catalyst activity maintenance. This problem is encountered in the petroleum processing area as well, and there has been increasing concern over the last few years about the effect of metals and minerals such as V and Na on the deactivation and regeneration of HDS catalysts. It is not clear to date, however, whether the effects are physical or chemical. In the case of deactivation, for example, metal accumulation with consequent blockage of pores may lead to activity loss even without a chemical interaction between the catalyst and the metal impurities. The problem is likely to be especially severe in coal conversion due to the presence of Ti (8). Certain coals have Ti concentrations as high as 0.06% (9). Using typical throughputs and catalyst loadings for a Synthoil pilot plant (10), for example, this concentration is equivalent to an accumulation of 2% of Ti on the catalyst per day. While it is unlikely that all the Ti will deposit on the catalyst, these figures are indicative of the magnitude of the problem.

The chemical effect of metals and minerals is most dramatically felt during regeneration. Indications from experiments with petroleum HDS catalysts suggest that only catalysts that have been exposed to low levels of minerals and metals can be oxidatively regenerated without irreversible loss in support surface area (8). The behavior of coal conversion catalysts has to be studied in more detail to identify possible sources of degradation and develop means to avoid it. In the preliminary work on the Synthoil process, for example, the partially solubilized coal is fed over the catalyst at high linear velocities, giving rise to some attrition of the catalyst surface. This is reported to prevent the accumulation of carbon and mineral matter. However, it is likely that

most cobalt molybdate catalysts will undergo uncontrolled attrition with extensive use. Recent developments in the area of catalyst preparation indicate that a number of additives may be available to reduce high attrition rates (11).

Another problem of regeneration that requires attention is the need to re-synthesize the active catalyst after it has been oxidized during the removal of carbonaceous residues. This places a limitation on the choice of catalytic materials, and a severe constraint on the structural integrity of the catalyst during repeated regeneration-reativation cycles. The concept of catalyst-support interactions discussed earlier (4) are pertinent to this problem. Some of the recently developed applications of this concept to NO<sub>x</sub> reduction catalysts illustrate the use of catalyst-support interactions in various chemical environments.

A problem common to any R & D program in coal liquefaction is the choice of test reactor system. This applies to the determination of activity, selectivity, and activity maintenance. An autoclave reactor, for example, is not suited for kinetic measurements, and often cannot be used effectively to discriminate between catalyst systems (12). The only exception is a low thermal inertia reactor capable of being heated and cooled rapidly. It can be an effective means of catalyst screening. The most versatile testing system, however, is a three phase continuous reactor. Several modifications of such reactors have been developed over the last few years (13), and can be used to obtain initial reaction rates, data concerning catalyst deactivation, and, if a high stirring rate is used, the effect of conversion levels on activity and selectivity.

## b. Stability

As discussed earlier, the determination of the extent of catalyst instability for existing liquefaction catalysts (primarily cobalt-molybdate on alumina) will require the development of characterization techniques which can measure the active catalyst surface area. These techniques may find utility for determining the extent of sintering and possibly even changes in chemical state for the active catalytic surface. The general area of catalyst-support interaction, discussed earlier, should play an important role in solving these problems.

In addition to the possible agglomeration of the catalyst on the support, HDS and HDN catalysts face the problem of support sintering. As mentioned above, the problem can be particularly severe during regeneration, especially in the presence of minerals and metals (8). In the last decade, a number of attempts have been made to stabilize supports. There are several cases in the patent literature that suggest, for example, that cationic doping has a pronounced effect on the thermal stability of  $Al_2O_3$  (14). Such results should be explored in connection with the stabilization of HDS and HDN catalysts. Other advances, including the development of ultrastable zeolites, are longer range developments and will be discussed in the next section.

The general study of sintering phenomena has gained increasing interest among catalytic chemists in the last decade. Sintering mechanisms are being developed for specific catalyst systems, and the effects of various environments are being evaluated (15). It has not been studied extensively in currently used HDS and HDN catalysts, partly because of the lack of thorough characterization. However, it is likely to become an important area in the future, with emphasis on special problems that are

specific to these systems. The fluxing effect of  $V_2O_5$  on HDS catalysts used in refining of residuum is a case in point. An additional problem encountered with vanadium in residuum refining catalysts is formation of  $SO_3$  during oxidative regeneration. This leads to sulfate formation of the support, with consequent phase change, surface area decrease, and mechanical degradation. The  $SO_3$  formation is catalyzed by  $V_2O_5$ . This is unlikely to occur in the presence of  $TiO_2$  due to the high stability of the sulfate (16, 17). However, the possible effect of other mineral matter in coal should be considered.

## 2. LONG TERM DEVELOPMENTS

Eventually, new catalysts will have to be found to overcome the activity, selectivity (hydrogen consumption and liquid yield), and stability limitations of current processes. A number of developments that are likely to impact in this area are examined in this section. For convenience the discussion is divided into parts, reviewing novel preparative procedures, new catalytic materials, and novel concepts and techniques, respectively.

### a. Novel Preparative Procedures

As discussed earlier, the properties of the support play an important role in the behavior of the catalyst. This includes physical properties such as pore size distribution and chemical properties such as acidity. A number of preparation procedures which have been reported in the last few years are of interest. For example, gel procedures for the synthesis of supports with controlled surface acidity (18) provide a means of systematically varying this important property of liquefaction catalysts. Similarly, novel preparations of supports with controlled crystallite size and pore size distribution (19) are going to be increasingly important in liquefaction. Finally, innovative procedures for the preparation of components of mixed oxides with ultrastable zeolites

reported in the last few years (20) provide compositions of interest for coal liquefaction catalysis. There are indications that these coprecipitated systems have very high HDS and HDN activity (20).

b. New Catalytic Materials

In Part 2, a general overview of inorganic chemistry was provided. As shown there, and developed in more detail elsewhere (21), the presence of high  $H_2S$  concentrations in coal liquefaction places a stringent constraint on the materials that can be suggested for liquefaction catalysis. The few groups that are most promising include oxides, oxysulfides, sulfides, and select members of other families of compounds.

In recent years a number of complex oxides and sulfides have been synthesized and characterized. Many of them exhibit interesting structural characteristics such as the metal-metal clusters of molybdenum in  $Al_{0.5}Mo_2S_4$  (22) and  $Mg_2Mo_3O_8$  (23). Most importantly, some of these have been synthesized in very high surface areas (18), thus making them readily amenable to catalytic studies. The possibility of stabilizing valence states such as  $Mo^{4+}$  in a complex oxide matrix, and the possible change in oxidation state due to Mo-Mo cluster formation, may have significant effects on the catalytic properties of these materials. Oxysulfide formation in these systems may be particularly important for liquefaction, especially in view of recent observations that the addition of oxygen to currently used HDS catalyst during reaction increases the activity (24).

The effect of oxygen on the reaction is very different in the case of HDN (25). The mechanism of HDN is also believed to be different from HDS, and so are the optimum catalysts. The optimum Co/Mo ratio, for example, is different for these two reactions (26). New catalysts have to be developed for HDN. They will have to survive, however, the high  $H_2S$



environment of the process. Possible designs that incorporate a sequential process with two catalyst beds optimized for HDS and HDN, respectively, should be considered. Similarly, a multifunction system incorporating the two optimum catalysts should be designed and tested.

c. Novel Concepts and Techniques

One of the important problems of coal liquefaction is coal-catalyst-hydrogen contacting. As expressed in the introduction, in most processes the coal is dissolved by a hydrogen-donating liquid which in turn is re-hydrogenated at the catalyst surface. Recent observations suggest that the nature of the coal dissolution is crucial in minimizing hydrogen consumption (27). This work indicates that the coal structure is not as aromatic in nature as one would deduce from the analysis of conventionally-produced coal liquids. Indeed, the aromatic structures consist of significant numbers of one, two, and three ring aromatic and naphthenic units interconnected by paraffinic structures (methylene groups). The latter are believed to participate in condensation reactions during the usual liquefaction processes. Thus, much of the asphaltinic nature of coal liquids may be generated during dissolution by polymerization and condensation reactions. This is in good agreement with at least one contemporary theory of the structure of coal, namely that by Chakrabarty which suggests a significant amount of  $sp^2$  and  $sp^3$  carbon. A technique that may improve coal dissolution is the use of supercritical solvents (28). While only limited work has been done in this area, there is evidence of improved coal extraction (29) and a considerable increase in hydrogen solubility, both factors of importance in coal liquefaction.

In the previous section, catalyst characterization was stressed as being an important problem in coal liquefaction catalysis. In particular,

the development of specific surface area measurement techniques is considered an urgent problem. Another important aspect of characterization is the use of spectroscopic techniques for surface analysis. A number of promising techniques have been studied in the last few years (30). However, a longer range development effort is required before many of these techniques can be applied routinely. Among the most promising and pertinent techniques are the electron spectroscopies, primarily Auger and x-ray photoelectron spectroscopy (31); the ion spectroscopies such as ion scattering spectroscopy (ISS) and secondary ion mass spectroscopy (SIMS) (32), and the recently developed x-ray absorption fine structure spectroscopy (EXAFS) (33) which promises to provide unique information about the local structure and environment of surface atoms in highly dispersed systems. One particular advantage of the ion spectroscopies is their ability to detect hydrogen (34), an important constituent of surface residues on liquefaction catalysts. However, as discussed in Part 2, all of these techniques have limitations which need to be overcome before they can be applied routinely.

### 3. SUPPORTING RESEARCH

As mentioned in the introduction, the primary aspects of this study relate to the impact of catalysis and related disciplines on the development of new and improved liquefaction processes. However, there are a number of additional areas discussed in Parts 1 and 2 which would lead to a better understanding of the phenomena involved in coal liquefaction, and therefore complement the developments and concepts highlighted above. These are briefly summarized in this section. It is convenient to separate activity and selectivity from stability related programs.

a. Activity and Selectivity

Catalyst improvements often benefit directly from an understanding of the reaction mechanism involved. Reactions of importance to coal liquefaction are HDS, HDN, and polynuclear aromatic cracking. They were discussed in detail in Part 1, where it was noted that while HDS has received considerable attention in the last few years (35), this is not the case for HDN (36). The evidence indicates that these two reactions have considerably different rate determining steps, and it is therefore not surprising that the best catalysts for these reactions are not the same. More studies are needed to relate the difference in mechanisms to the difference in catalyst requirements. Studies that are particularly interesting in this respect involve the effects of simple gaseous molecules such as  $O_2$ ,  $H_2S$ ,  $CO$ ,  $CO_2$ , and  $NH_3$  on the activity and selectivity of HDN and HDS reactions.

As discussed earlier, preliminary results suggest that oxygen plays a more important role in HDS compared to HDN (24, 25). The formation and behavior of oxysulfides may therefore be of great importance to the former reaction, as discussed in the earlier sections. Studies of the thermodynamics of oxysulfide formation, the stability of oxysulfides in high  $H_2S$  concentrations, and the structural integrity of oxysulfides after repeated reaction-regeneration cycles should be emphasized. Similarly, the balance between increased sulfiding resistance and the changes in HDS/HDN activity of catalysts should be examined.

As discussed in Part 1 (37), the effect of particle size on the activity and selectivity of catalysts has received considerable attention in the last decade. However, as also pointed out (38), the effects of particle size are usually less important than the effect of variations in

catalytic materials. For sulfide catalysts, on the other hand, there are indications that the edges of particles, and thus particle size, may have a profound effect on the activity (39). These conclusions follow from a systematic study of the hydrogenation activity and physico-chemical properties of the nickel-tungsten sulfide system. It has not been extended to other systems, nor has it been applied to HDS or HDN reactions. It does, however, point to an area that may be important in the optimization of catalysts for these processes.

b. Stability

In the discussion of short and long term developments needed to obtain more stable catalysts, new materials were stressed. Unfortunately, not much is known about the stability, in particular chemical stability, in  $H_2S$ , of a number of classes of inorganic compounds. This was illustrated, for example, in the discussion of borides, phosphides, and silicides (40). There is therefore a definite need for more information on the thermodynamics of such compounds in the presence of gases expected during liquefaction and regeneration, primarily  $H_2S$  and  $O_2$ . The discussion on inorganic chemistry in Part 2 highlighted a large number of materials. Preliminary examination of their stability in  $H_2S$  indicated that only few compounds would resist sulfidation. They included borides, phosphides, and silicides of the Group VIII metals (41), certain select nitrides (42), and select oxides (43). More thermodynamic and kinetic information is needed for these compounds.

D. CONCLUSIONS

A number of developments in catalysis and related areas are likely to play an important role in the improvement of the catalytic liquefaction of

coal to boiler fuels. Some of these developments have immediate implications for the improvement of existing systems. Others are going to be important in the search for new catalysts and processes.

Of particular importance in the short term development are techniques for the measurement of the surface area non-metallic catalysts. Such characterization techniques have implications for efforts to study and improve catalytic activity, to identify the role of the catalyst and the support, and to establish the importance of catalyst sintering processes during reaction and regeneration. Other areas that should be stressed include optimization of the pore size distribution of the catalyst to minimize deactivation, modifications of the support to improve attrition resistance, and greater emphasis on overcoming catalyst regeneration problems and the low HDN rates encountered in currently used liquefaction processes. For the latter it is important to perform activity studies with real feeds since competitive adsorption may substantially change the behavior observed with model compounds. Among the long term developments, the application of novel preparative procedures and catalyst formulations are likely to have the most dramatic impact. Included in the latter are new catalytic materials, in particular complex oxides, sulfides, and oxysulfides. These developments should be complemented by more fundamental studies of the mechanisms of reactions of interest, especially HDN. These advances will also require more information concerning the thermodynamic properties for many of the catalytic materials of interest, particularly in the presence of reactive environments such as  $H_2S$ .

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