

DIRECT COAL LIQUEFACTION: DISTINCTION BETWEEN REACTANTS  
AND CATALYSTS

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INTRODUCTION

An extensive research and development program on disposable catalysts and slurry catalysis was supported by the Fossil Energy Office of the U.S. Department of Energy (DOE) during the period 1978-82. Actually, prior to 1978, a project of similar nature was carried out for several years, at a low priority effort, at the U.S. Department of Interior, Bureau of Mines laboratories which is now known as the Pittsburgh Energy Technology Center (PETC).

Although numerous slurry-phase catalysts were tested in this program, two metals, iron and molybdenum, in their sulfided form, were singled out as the most promising candidates for scale-up processing.

In 1982, Gray and Neuworth (1) and in 1983, Davidson (2) have made comprehensive reviews on the role of iron sulfides on coal liquefaction, and, up to the present, there has been a continuing level of activity in this area. Iron and molybdenum sulfides catalysts were amply covered in a very recent comprehensive and critical review on catalysis in direct coal by Derbyshire (3). This excellent review provides a current state of knowledge of all form of catalysis which are potentially of interest from a practical standpoint, in addition to give valuable new directions for research in this area.

Garg and Givens (4) have shown evidences of synergism for an Iron-Molybdenum catalyst in which mixed catalyst has a definite advantage over each individual metal preforming. Similarly Gatsis (5) uncovered a distinct synergism occurring for an Iron-Vanadium catalyst which permits the partial replacement of the expensive Vanadium with the low cost Iron, with no loss of the catalytic activity level.

The aforementioned references report that iron sulfides catalysts exhibit consistently lower hydrogenation activity than either the molybdenum or the vanadium sulfides. Various explanations were attributed to the low catalytic activity of the iron sulfides, such as the very low surface area and the variable catalytically active iron sulfides forms found in pyrites, the precursors present in the mineral matter of most coals.

This paper, presently in the form of a communication to be complemented by the oral presentation and to be expanded for publication in Energy and Fuels, intends to provide evidences that the active forms of iron sulfides have a different function than the other metal sulfides, the function of being reactants and catalysts.

An additional objective of this paper, in conjunction with a series of papers presented by this author in recent years (6), is to stimulate the research community, dedicated to coal liquefaction fundamentals, to undertake a more systematic research approach to discriminate the critical reactions from the numerous ones occurring particularly the lower temperature range, which, in turn, profoundly affect the subsequent reactions occurring at the higher temperatures.

#### INITIAL STAGES OF COAL LIQUEFACTION

This author (7) has stressed the importance of reactions involving heteroatom-containing compounds in coal dissolution and subsequent coal liquid upgrading. of the three major heteroatoms present in coal, the most abundant is the oxygen, and, particularly when it is in the form of carboxylic and phenolic species, it seems to dominate the reactions occurring in the initial stages of liquefaction. Except for the low-rank coals, in which the carboxylics are converted at the temperature range of 250-300°C, with the observed loss of CO<sub>2</sub>, the phenolic chemistry appears to dominate the reactions occurring in the 280-350°C temperature range, for coals of all ranks, except, perhaps, for the low-oxygen german's hard coal. In particular, the phenols are the major contributors for the regressive reactions, causing the high viscosity of coal liquids and increasing the difficulty of upgrading and refining, and, as discover in recent work, the promoters for catalyst deactivation. Lemberston et al.(8) tested a sulfided nickel-molybdenum on alumina catalyst for the hydrogenation/hydrocracking of a mixture of phenanthrene, carbazole and 1-naphtol, and discovered that the catalyst maintain its activity in the presence of the phenanthrene-carbazole mixture, but it is strongly deactivated when 1-naphtol is added to that mixture. This experimental evidence of catalyst deactivation promoted by the phenols confirms the intuitive thoughts emerged some ten years ago

from the experimental data provided by Suntech (9) by which the removal of the phenols from a SRC II distillate solvent caused a seven-fold increase in the kinetics of nitrogen removal by catalytic hydrogenation. At a later date, Garg et al. (10) used a defunctionalized solvent in which most of the phenols and nitrogen compounds were removed from a SRC I process solvent, and obtained high conversion and oil yield with only 0.2-0.5 weight percent addition of pyrite to the coal/solvent slurry. When the untreated solvent was used for comparison, addition of 3-5 percent pyrite was required to obtain the same conversion and oil yield.

The obvious thought, derived from this data, was that a large portion of the active iron sulfide reacted with the oxygen moieties with the loss of catalytic activity, and, only the excess pyrite functioned as the actual catalyst. To prove this point, the work of Montano (11) indicated a strong affinity of an active iron sulfide surface towards oxygen in which the carbon-oxygen bonds are broken even from very stable aromatic ethers to generate aromatic hydrocarbon and catalytically inactive forms of iron sulfate or oxide.

The removal of oxygen moieties from coals, in the initial and subsequent stages of liquefaction, by the reaction with inexpensive iron sulfides, whose precursors happened to have the good fortune of being the most abundant components of the mineral matter in coal, ought to be considered highly desirable from the economic and technological point of view.

#### CONCLUSIVE REMARKS

Derbyshire (3), in his review on catalysis for coal liquefaction, questioned the modest progress obtain in catalytic liquefaction, particularly when research in this field has been conducted for half a century. Absence of a realistic model coal structure, and, of a clear understanding of the reaction chemistry and, the cyclic nature of interest in research of coal liquefaction were the main reasons for the impediment of progress in catalysis, according to Derbyshire.

The data and thoughts presented in this communication seem to complement Derbyshire's assessment, in that the scarce progress in catalytic liquefaction is due to the fact that catalyst activity is more dependent on the feed composition in contact with the catalyst than on the catalyst formulation. Preconversion treatments to remove first the active oxygen species is necessary prior to submit coal-derived extracts to supported catalysts for further conversion to environmentally acceptable fuels.

This suggests that the research approach in coal liquefaction ought to be systematic because there is the likelihood of significant complex relationships between coal structure, reaction mechanisms, thermodynamics, analytical chemistry, kinetics and, finally, catalyst selection.

## REFERENCES

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