Bifunctional Transition Metal-Zeolite Catalysts For Synthesis Gas to Gasoline Conversion

I. INTRODUCTION

A. General

The production of petroleum feed stocks chemical intermediates and speciality chemicals from synthesis gas (hydrogen plus carbon monoxide) has received substantially increased attention from the chemical and fuel industries over the past decade. The research and development effort expended in the area of synthetic fuels technology has been accelerated by the 1973 Arab oil embargo spiraling oil prices, dwindling supplies of endogenous petroleum, and the existence of massive Western coal reserves. The certainity of long-term crude shortages coupled with the short-term shortages of socio-political origin promise devastating consequences to Western civilization as we know it. The development of synthetic liquid fuels utilizing the extensive energy reserves possessed by the United States in the form of coal is as important, if not more important, in protecting our way of life as the maintenance of national defense. Despite the significant progress which has been made in the past decade in developing new and better processes to produce petrochemical feed stocks, the conglomerate funding both private and federal can be characterized as 'too little, too late.' The disproportionate allocation of resources by Congress which has minimized the development of synthetic fuels in preference of the Department of Defense, is analogous to Chase Manhatten allocating all of its resources to the purchase of a vault and security system so extensive and safe that there is no cash left in the vault to protect. We have been inoculated one hundred times against small pox but are dying of polio.

Three technologies presently exist for converting coal to liquid fuels; i.e., pyrolysis, direct hydroliquefaction, and indirect liquefaction. In indirect liquefaction the structure of coal is first destroyed through the gasification of coal by reaction with steam and/or oxygen. The resultant gases, hydrogen and carbon monoxide, can be converted into chemicals, gaseous fuels or sulfur-free liquid transportation fuels by a variety of catalytic processes. A summary of the technology of gas manufacture from solid and liquid fuels is given by Kirk-Othmer.[1] An excellent review of the synthesis of transportation fuels by way of indirect coal liquefaction is given by Schehl.[2] The generalized process of indirect coal liquefaction presented by the latter author is shown in Figure 1.[2] The most significant factor in determinining

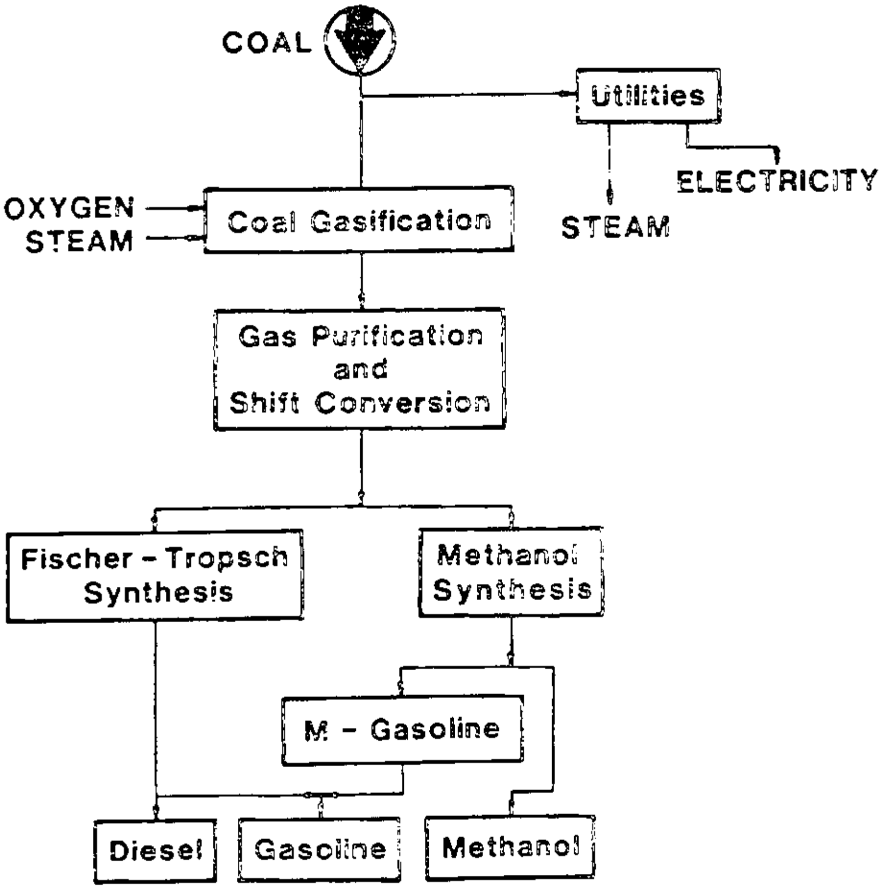

Figure 1- Generalized indirect coal liquefaction process.[2]

the cost effectiveness in the production of fuels and chemicals from synthesis gas is the performance of the catalyst in this catalytic conversion. The reduction products of carbon monoxide, i.e., hydrocarbons were first observed in 1902 [3] by Sabotier and Senderens who reported the synthesis of methane from synthesis gas over a reduced nickel catalyst. This marked the origin of indirect liquefaction. The synthesis of higher molecular weight hydrocarbons was first reported by Franz Fischer and Hans Tropsch in 1923 using an alkalyzed iron catalyst.[4] The first large scale Fischer-Tropsch plant was built by Ruhrchemie at Sterkrade-Holten in 1935.[2] By 1943 nine additional indirect liquefaction plants produced 15% of the total German synthetic fuels production (the balance being high pressure direct hydrogenation).[2] Following this period, the production of hydrocarbons from synthesis gas via the Fischer-Tropsch process decreased and to date, the only commercial operations utilizing this technology are at Sasol (South African Coal, Oil, and Gas Corporation). Contributing to the decline of Fischer-Tropsch synthesis is the inherent non-selective product distribution characterized by the Schulz-Flory polymerization method. Methane is the only hydrocarbon which can be produced with 100% selectivity. When gasoline is synthesized on conventional Fischer-Tropsch catalysts, a substantial fraction of the hydrocarbons produced exceed 12 carbon atoms per molecule and have boiling points too high to be useful as gasoline fuels. If the process variables in a F-T reactor are adjusted to minimize the production of C_{12}^{+} hydrocarbons, large amounts of light gases i.e., C_1 to C_5 hydrocarbons are formed. Even under the optimum operating conditions for the synthesis of gasoline on Fischer-Tropsch catalysts more than half of the hydrocarbon yield falls outside of the gasoline range. The result of this is that costly secondary treatments are required to crack the C_{12}^{+} fraction into the gasoline range and to reform the C_5^{-} fraction to this range. The economic burden of these secondary treatments prevent the manufacture of gasoline by this technology in a free society. It would not exist in South Africa if not for the extensive subsidy provided by the South African Government.

The development of novel shape-selective zeolite catalysts known as zeolites promises to circumvent The limitations placed on the product distribution by the Schulz-Flory polymerization mechanism. Zeolites are hydrous framework aluminosilicates which have been extensively employed in the chemical and fuel industries over the past 20 years. The most notable of their applications in terms of the economic impact has been in their application to catalytic cracking. Catalytic cracking provided the means through which the composition of crude could be catalytically altered to be in harmony with the refined product demand. The application of zeolite cracking catalysts has been estimated to save refiners over $250,000,000 per year over the older amorphous forms.[5]

The development of new high silica pentasil zeolites by Mobil Research and Development Corporation has provided catalytic routes to improve both the total liquid yield of the Sasol-Synthol process and to upgrade the quality of the gasoline fraction. Two new approaches have emerged in the conversion of synthesis gas to hydrocarbons. In the first approach a CO reduction function (Fischer-Tropsch catalyst) is combined with a Pentasil family zeolite such as ZSM-5. The shape-selective zeolite component, i.e., ZSM-5, functions to reduce the C_{12}^{+} hydrocarbon fraction and simultaneously increase the octane rating of the gasoline fraction. The latter is accomplished through the synthesis of higher concentrations of branch-chained and aromatic hydrocarbons.

In the second approach, synthesis gas is first converted to methanol over a methanol synthesis catalyst and methanol subsequently polymerized to hydrocarbons over ZSM-5. The first approach resembles the Sasol process shown in Figure 2 [2] except the Synthol step takes place over a bifunctional catalyst rather than a conventional Fischer-Tropsch catalyst. The second approach shown in Figure 3 is known as the Mobil M process.[2]

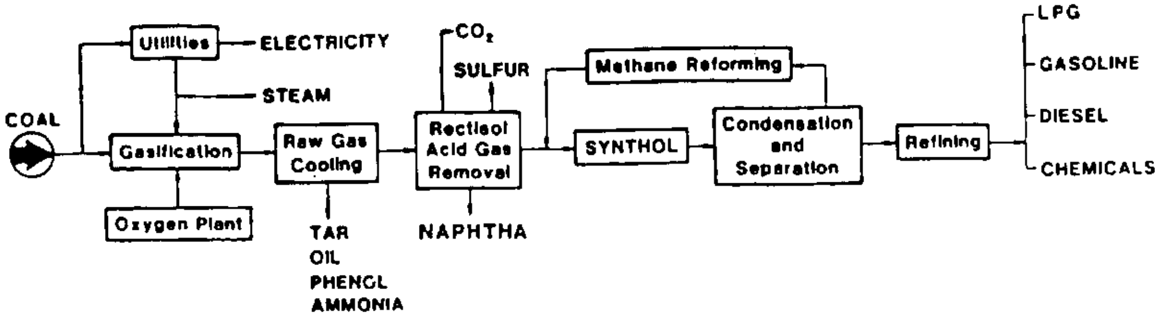

Figure 2- SASOL Fischer-Tropsch synthesis

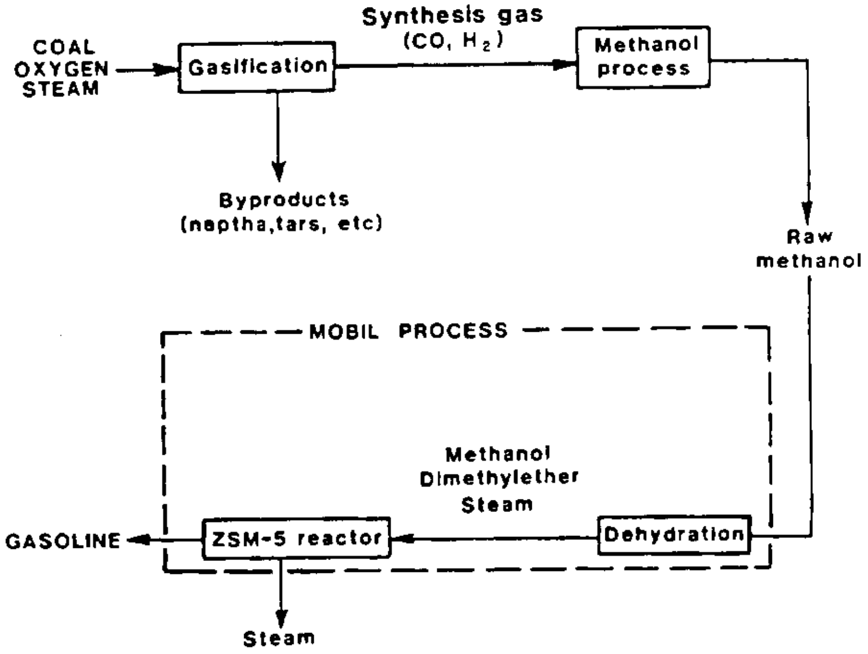

Figure 3- Mobil m-gasoline process .

B. Objectives of Study

The purpose of this study is to investigate bifunctional zeolite based catalysts in the conversion of synthesis gas to gasoline. To facilitate this investigation the first goal of this research effort was to design and implement a fully computerized research laboratory to be used to characterize various types of bifunctional STG catalysts (Synthesis Gas to Gasoline).

The second objective of this research was to attempt to produce catalytic bifunctionality through the incorporation of the CO reduction function (a transition metal) during the synthesis of a shape selective zeolite (ZSM-5). Conventionally, bifunctional catalysts are prepared by the impregnation of a zeolite catalyst with a transition metal using the insipient wetness or carbonele impregnation techniques. In insipient wetness impregnation a solution containing a soluble salt of the desired transition metal is contacted with the zeolite support. The liquid phase is removed by evaporation and the resulting catalyst reduced into its catalytically active form.

In carbonyl impregnation a volatile metal carbonyl is adsorbed and/or into the molecular sieve zeolite. The catalyst is then heated to the decomposition temperature of the metal carbonyl at which time carbon monoxide is evolved and the metal deposited on the zeolite surface.

The direct synthesis approach places the CO reduction function in the hydrothermal solution from which the zeolite is crystallized. If the presence of the transition metal within this hydrothermal magma does not prevent the crystallization of the zeolite, it is possible the zeolite thus formed might have occluded salts of the transition metal during synthesis. Metal so occluded would be highly dispersed and might give rise to unique catalytic properties.

The final objective is to employ the laboratory designed in objective 1 to evaluate the catalytic performance of the unique class of bifunctional transition metal catalysts described in objective 2. The effectiveness, i.e., degree of conversion and selectivity to the gasoline range can then be compared to conventional bifunctional catalysts in the conversion of synthesis gas to gasoline.