SUMMARY

I. Iron-Based Catalysts for Coal Liquefaction

Research on sulfate and metal(Mo, Sn) promoted Fe_2O_3 catalysts[1,2] in the current year focused on optimization of conditions. Parameters varied included temperature, solvent, solvent-to-coal ratio, and the effect of presulfiding versus in situ sulfiding. Oil yields were found to increase approximately proportionately with both temperature and solvent-to-coal ratio. The donor solvent, tetralin, proved to give better total conversion and oil yields than either 1-methylnaphthalene or Wilsonville recycle oil. However, the oil yield obtained using the Wilsonville recycle oil was almost as large as that using tetralin. In situ sulfiding gave higher yields than presulfiding the catalyst to pyrrhotite before liquefaction. Model compound reactions at relatively mild conditions(160-200 °C, 300-500 psig H_2) established that superacidity of anion-modified iron and tin oxide catalysts plays an important role in hydrocracking and alkylation of 1-phenyldecane.

A significant enhancement of both total liquefaction yields and oil yields from lignites and subbituminous coals has been achieved by incorporating iron into the coal matrix by cation exchange[3,4] In this process, the iron enters the coal molecularly, replacing calcium cations bound to the oxygen anions in carboxyl groups. Mossbauer spectroscopy indicates a bimodal size distribution, with ~20-40% of the iron present in particles <25 Å in diameter, which may represent molecularly dispersed iron, and the balance contained in particles 50 to 100 Å in mean diameter. In recent experiments, it was shown that the cation-exchanged iron had significantly greater catalytic activity for liquefaction than the 30 Å Mach I catalyst.[3,4]

A systematic study of the catalytic properties of the 30 Å iron oxyhydroxide (ferrihydrite) catalyst produced by Mach I, Inc. was carried out.[5] Liquefaction studies of four coals were carried out and a number of model compound reactions were investigated. The coals investigated included Blind Canyon(DECS-6) and three Argonne premium coals, Illinois #6, Pocahontas #3, and Wyodak.For Blind Canyon coal, the effect of different solvents, catalyst loading, and the presence or absence of added sulfur were investigated. All four coals were liquefied at two temperatures both with and without the 30 Å catalyst plus added sulfur. All coals exhibited significant liquid yield improvements with the added catalyst, particularly Pocahontas #3, for which oil yields tripled, and total liquid yield more than doubled at 400 °C. The reduced catalyst, presumably to iron metal, showed much greater

activity for the hydrogenation of naphthalene than the sulfided catalyst. The activity decreased with reduction temperature, presumably due to catalyst sintering.

An aerosol reactor for the production of fine particle catalysts was constructed and tested. Mixtures of pyrite(PY) and pyrrhotite(PYH) were produced using a fuel injector to inject ferric acetate solution into a reaction chamber containing a nitrogen/hydrogen sulfide mixture at a pressure of 200 psig and temperature of 200 °C. In related work, PY/PYH catalysts were produced by hydrothermal disproportionation of ferric sulfide under a wide range of conditions. The aerosol product is a thin-shelled hollow sphere of catalyst made up of fine particles ~0.1 to several microns in diameter. These catalysts exhibited good catalytic activity in the liquefaction of Blind Canyon coal[6,7] and in preliminary coliquefaction experiments on rubber tire tread material and coal.

A systematic investigation has been conducted of the synthesis of 5 - 20 nm diameter Fe-, Mo- and W-based particulate catalysts using a CO_2 laser pyrolysis technique. These catalysts include carbides (Fe_3C, Fe_7C_3, Mo_2C, W_2C), sulfides ($Fe_{1-x}S$), nitrides (Fe_3N, Fe_4N, Mo_2N, W_2N), oxides (Fe_3O_4,WO_3), and metals (α-Fe, γ-Fe). Commercial carbonyl compounds including $Fe(CO)_5$, $W(CO)_6$ and $Mo(CO)_6$ have been used as chemical precursors, and C_2H_4, H_2S, NH_3, and O_2 as reactant gases. The catalytic benefit of nanoscale Fe-carbide (Fe_7C_3) and Fe-sulfide ($Fe_{1-x}S$) catalysts produced by laser pyrolysis in the direct liquefaction of subbituminous coals has been investigated.[8,9] The results have been compared to those determined for commercial Fe-oxide catalysts.

The CO_2 laser pyrolysis method has been extended to synthesize nanoscale carbon black particles, which might be used as catalysts or as a catalyst support for more expensive metals (e.g., Pt, Mo, etc) in coal liquefaction. These carbon particles are produced by pyrolyzing benzene (C_6H_6) with a small amount of $Fe(CO)_5$ as a catalyst. Furthermore, using our laser pyrolysis system, we have produced $FeWO_4$ by pyrolyzing a mixture of $Fe(CO)_5$, $W(CO)_6$, and O_2, which demonstrates for the first time that the CO_2 laser pyrolysis is also useful to produce stoichiometric, crystalline, and nanoscale *ternary* compounds. This is important since many mixed-valence ternary compounds (e.g. $La_{2-x}Sr_xCuO_4$) have been found to exhibit high catalytic activity.

The activity and selectivity of iron-based slurry-phase catalysts were investigated for the hydrogenation of pyrene and the hydrocracking of C-C bonds in several model compounds: 1-methylnaphthalene (1-MN), 2-hexylnaphthalene (2-HN), and 4-(1-naphthylmethyl-bibenzyl (NMBB).[10] Reactions ere performed under typical coal liquefaction conditions. Higher reaction temperature and the presence of sulfur increased the hydrogenation of pyrene by the iron catalysts generated in situ. An in situ method of catalyst addition was most effective for pyrene hydrogenation for the iron catalysts, while molybdenum naphthenate showed increased activity with two-

stage processing. Both Fe and Mo catalysts showed low activity in reactions where the catalyst was generated ex situ. Combinations of Fe and Mo catalysts were synergistic for pyrene hydrogenation, although the amount of increase was dependent upon the particular iron precursor used. The Fe and Mo catalysts affected the hydrocracking of the three model species differently. Molybdenum naphthenate was more active for hydrocracking 2-HN and NMBB than any of the Fe catalysts but combining FeNaph with MoNaph was detrimental to the hydrocracking of these compounds. The selectivity of hydrocracking NMBB at specific bonding sites was affected by the presence and type of catalyst, presence of sulfur, and reaction time.

Water-soluble compounds containing molybdenum, tungsten, iron, cobalt and nickel were used as catalyst precursors for the catalytic hydroliquefaction of Blind Canyon coal in the absence of a solvent.[11] The coal was impregnated from solution, then vacuum dried at 55 °C and hydroliquefied in tubing bomb reactors at 400 °C, ~2,000 psi H_2. Tests of numerous iron and several nickel and molybdenum water-soluble catalyst precursors were completed using the same catalyst concentration(0.03 wt.%). Nickel hexahydrate and ammonium tetrathiomolybdate gave the best total liquid yields(~80%). While Mo gave the highest total liquid yield, the oil product was less volatile than that from Fe and Ni catalysts. This suggests that Mo is a good hydrogenation catalyst, but that Fe and Ni are better choices for hydrocracking of primary coal liquid products.

A number of methods of characterizing both the size and structure of iron-based catalysts have been fully developed.[12-18] A new method of analyzing low temperature superparamagnetic Mossbauer relaxation spectra has been developed that provides a novel approach to determining the size distribution of ferric oxide and oxyhydroxide catalysts.[12] For catalyst particles only a few nanometers in diameter, the recoilless fraction of the ^{57}Fe nuclei is markedly decreased by particle recoil on gamma ray absorption and by thermal agitation of the particles.[13] X-ray absorption fine structure (XAFS) spectroscopy provides information both on the electronic state and radial distribution of ultrafine particles.[14,18] Excellent TEM capabilities have been developed for direct measurement of size distributions and structure determination through electron microdiffraction.[15,18] Electron probe microanalysis has been used to study the dispersion of iron, molybenum and nickel in chemically impregnated coals and hydrotreated coals.[16] Iron was found to be more uniformly dispersed through the coal particles after hydrotreatment than either molybdenum or nickel. XAFS spectroscopy has established that the surface iron atoms of ultrafine ferrihydrite catalysts are coordinate unsaturated sites.[14] The tendency of these particles to agglomerate and transform to large particle hematite is dramatically increased by the chemisorption of water, as shown directly by TEM measurements of particle size distributions and structure.[15] Magnetization measurements from 5 K to 300 K in zero-field-cooled and field-cooled cases are used to determine the region of superparamagnetism for nanoscale iron oxide and oxyhydroxide particles, followed by magnetization measurements up to 55kOe in the superparamagnetic state to

determine the particle size distribution.[17] The use of all these methods, as well as more standard techniques such X-ray diffraction line broadening, has been compared in a comprehensive article summarizing a wide range of characterization studies for most the classes of iron-based catalysts under investigation in the Consortium.[18]

XAFS spectroscopy, transmission electron microscopy(TEM), and Mossbauer spectroscopy were to determine the structure of a 30 Å iron oxide catalyst manufactured by Mach I. It was found to have the ferrihydrite structure with coordinate unsaturated sites (CUS) at the particle surface.[14] Chemisorbed moisture at these sites drastically increases agglomeration and transformation to large particle hematite at elevated temperatures.[15] New ultrafine (~3-10 nm) binary ferrihydrite catalysts containing Si and Al have been synthesized using simple precipitation methods.[19] The Si is believed to occur as SiO_4 at the particle surfaces.

II. Novel Coal Liquefaction Concepts

A unique coal liquefaction reactor system has been developed.[20] The jet loop reactor system permits better control of free radical generation/reaction and offers higher mass transfer rates than conventional reactors. It is now being used for the coprocessing of coal with waste oil.[21] Improvements in conversion and selectivity are observed, relative to conventional reactors. The reactor provides a vehicle for evaluating coal slurries, coprocessing materials, and catalyst activity.

An investigation has been conducted of the comparative activity of soluble iron catalysts to that of solid iron catalysts in the multi-step Shabtai liquefaction procedure.[22] It was concluded that Fe_2O_3/SO_4 exhibited comparable activity to aqua complexes of salts such as $Fe_2(SO_4)_3(H_2O)_5$ and $FeCl_3(H_2O)_6$. Such solid nanoscale iron-based catalysts could therefore replace the soluble salts in the HT-BCD step of the treatment.

A high pressure(5-500 psig) multipurpose bioreactor was constructed and tested. A study with *D. desulfuricans* under normal and high pressure H_2 showed complete(~100%) reduction of fumarate within 24 hours.[23] Mossbauer spectroscopy verified the formation of ultrafine FeOOH from pyrite in coal by treatment with *Acidianus brierleyi*. The liquefaction yield was increased by this treatment by 14%.

A novel continuous-flow semi-batch liquefaction reactor has been designed and successfully tested. The advantage of this reactor over a batch liquefaction reactor is that light liquefaction products produced in the former can be removed by the flowing H_2, preventing further cracking or condensation reactions.

III. Fundamental Studies in Coal Liquefaction

A rapid HPLC method has been developed for separating the oil fraction of coal-derived liquids into aliphatic, aromatic and polar molecules.[24] Product concentrations are determined with an evaporative light scattering detector. Product fractions have been collected and concentrated for further analysis using GC/MS and SFC/MS methods.

Systematic procedures were developed for optimal waste management systems for coal liquefaction processes.[25] These procedures were used to identify cost effective solutions for two major environmental problems associated with coal liquefaction; desulfurization of gaseous emissions and dephenolization of aqueous wastes. The most cost-effective methods identified are desulfurization by hot potassium carbonate and a membrane-hybrid system for dephenolization. These methods have cost advantages over competing options that range from factors of ~ 3 to 10. The major source of CO_2 in a coal liquefaction plant is the Claus unit which converts H_2S to elemental sulfur. It is found that the cost of reducing CO_2 emissions to 500 ppm is almost negligible (~$0.1 - 0.2/bbl), but the cost of achieving emissions limits ~10ppm is prohibitive (~$10 - 15/bbl).

The ^{13}C NMR research program of the CFFLS has focused in the current year on the development of two dimensional(2D) methods.[26,27] Equipment has been constructed to perform a new class of experiments, referred as magic angle turning(MAT), involving very slow spinning at the magic angle. With the MAT experiment, the average or isotropic chemical shifts are obtained in one dimension and the separated powder patterns are found in the second dimension. This greatly increases the number of tensor components that can be extracted from the spectrum, thereby increasing the complexity of the samples that can be studied. This method has been applied to the Argonne premium coals with excellent results. In future work, it will be applied to polymeric waste material and to the products of coliquefaction of coal with such waste material.

In situ ESR studies have demonstrated a clear relationship between the addition of nanoscale iron-based catalysts and the free radical density.[28] Hydrocracking activity is evident from the formation of more free radicals at lower temperatures in the presence of such catalysts at temperatures up to ~400 °C in hydrogen. New experimental capabilities that have been developed and are now starting to be explored are the capability of high pressure, high temperature, in situ ESR, and the ability to add a catalyst, solvent or other reactant in situ during the ESR measurement.

An investigation of the catalytic dehydrogenation(CD) of coal and recycle solvents is being conducted to achieve insights into the chemistry of direct coal liquefaction(DCL) and to see whether CD can be used as a method for assessing the

activity of DCL catalysts.[29] Hydrogen transfer ability of different solvents by catalytic reaction with a hydrogen acceptor such as stilbene. Pyrrhotite was observed to be about six times less active than MoS_2 for catalytic dehydrogenation of 9,10-dihydroanthrancene. This is approximately the ratio of the activities of these phases for DCL.

The development and testing of the high pressure TG/GC/MS system has been completed and several studies have been performed on coals, model polymers and waste polymers at hydrogen pressures up to 900 psi and with various catalysts provided by several Consortium members (viz. Professors Anderson, Shabtai and Wender).[30,31] These experiments are starting to provide a wealth of new information on the mechanisms of heterogeneous catalysis, e.g., with regard to the role of radical vs. carbonium ion chemistry in hydropyrolysis or hydrogenolysis reactions and on the effect of hydrogen pressure and specific catalysts on hydrogasification (hydrogenation) reactions. The construction and testing of a microscale high pressure flow-through reactor coupled to a GC/MS system has been completed and the first on-line analyses of coal conversion products in a variety of different solvent environments at pressures up to 700 psi have been performed.

Molecular orbital calculations have been used to study the adsorption of toluene and 1-methylnaphthalene at various sites on FeS and related defect clusters and to calculate bond-breaking energies of the aromatic-aliphatic linkage.[32] As a preliminary explanation of the catalytic activity of FeS, it is proposed that the donation of electrons to the iron surface by the adsorbate leads to a decrease in the bond breaking energies relative to the gas phase.

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