

Executive Summary

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Background

Faculty and students from five universities (Kentucky, West Virginia, Utah, Pittsburgh and Auburn) are collaborating on a basic research program to develop novel C1 chemistry processes for the production of clean, high quality transportation fuel. An Industrial Advisory Board (IAB) with members from Chevron, Eastman Chemical, Energy International, Teir Associates, and the Department of Defense has been formed to provide practical guidance to the program. The program has two principal objectives.

1. Develop technology for conversion of C1 source materials (natural gas, synthesis gas, carbon dioxide and monoxide, and methanol) into clean, high efficiency transportation fuel.
2. Develop novel processes for producing hydrogen from natural gas and other hydrocarbons.

Some of the principal accomplishments of the program in its first two years are summarized below.

- ★ The addition of acetylenic compounds in Fischer-Tropsch synthesis is found to produce significant amounts of oxygenated products in FT diesel fuels. Such oxygenated products should decrease particulate matter (PM) emissions.
- ★ Nanoscale, binary, Fe-based catalysts supported on alumina have been shown to have significant activity for the decomposition of methane into pure hydrogen and potentially valuable multi-walled carbon nanotubes.
- ★ Catalytic synthesis processes have been developed for synthesis of diethyl carbonate, higher ethers, and higher alcohols from C1 source materials. Testing of the effect of adding these oxygenates to diesel fuel on PM emissions has begun using a well-equipped small diesel engine test facility.
- ★ Supercritical fluid (SCF) FT synthesis has been conducted under SCF hexane using both Fe and Co catalysts. There is a marked effect on the hydrocarbon product distribution, with a shift to higher carbon number products.

These and other results are summarized briefly below.

Effect of Probe Molecules on Oxygenated Products in Fischer-Tropsch Synthesis

(Full report – pages 4-8)

It is reported that particulate matter (PM) emission reductions of 4-10% can be achieved for every 1% of oxygen blended into diesel fuel. In this project, the production of oxygenated diesel fuels by modifying Fischer-Tropsch (F-T) catalysts and reaction conditions is being investigated. The addition of acetylenic molecules, specifically 1-

and 2-hexyne into the F-T synthesis with iron and cobalt catalysts to produce oxygenated products is reported here.

1-Hexyne is readily incorporated into the F-T reaction to produce heptanol, heptanal and C8+ straight chain alcohols. In the case of 2-hexyne addition, a large amount of branched C7+ oxygenates are produced. At lower temperatures, these hexynes initiate chain-growth in the FT reaction and produce mainly C7+ products. The mode of incorporation of acetylenic molecules into F-T reactions is under investigation.

Production of Hydrogen and Carbon Nanotubes by Catalytic Decomposition of Methane (Full report – pages 13-19)

Traditionally, hydrogen has been produced by reforming or partial oxidation of methane to produce synthesis gas, followed by the water-gas shift reaction to convert CO to CO₂ and produce more hydrogen, followed in turn by a purification or separation procedure. This research is investigating the direct catalytic decomposition of undiluted methane into pure hydrogen and carbon using nanoscale, binary, Fe-M catalysts (M = Pd, Mo, and Ni) supported on alumina [(4.5% Fe – 0.5%M)/Al₂O₃]. All of the supported Fe-M catalysts reduced methane decomposition temperature by 400-500 °C relative to non-catalytic thermal decomposition and exhibited significantly higher activity than Fe or any of the secondary metals (Pd, Mo, and Ni) supported on alumina alone. At reaction temperatures of approximately 700-800 °C and space velocities of 0.1 per hour, the product stream was comprised of over 85 volume % of hydrogen, with the balance being unconverted methane. No C2 or higher hydrocarbons were observed in the product gas.

High resolution SEM and TEM characterization established that almost all carbon produced at 700-800 °C is in the form of potentially useful multi-walled nanotubes. At somewhat higher temperatures (> 850 °C), hydrogen production is decreased and carbon is deposited on the catalysts in the form of amorphous carbon, carbon flakes, and carbon fibers.

Supercritical Fluids as a Reaction Medium for Fischer-Tropsch Synthesis (Full report – pages 20-24)

Supercritical Fluids (SCFs) offer several advantages over traditional solvents as reaction media for catalytic reactions. Advantages of SCF-phase Fischer-Tropsch synthesis (SCF-FT) include high diffusivity and improved heat transfer (relative to a liquid) and high solubility (relative to a gas). In this investigation, FT synthesis has been conducted under SCF hexane conditions in a continuous, high-pressure reactor employing traditional Fe and Co catalysts (e.g., 15%Co-0.5%Pd/Al₂O₃). Steady state operation was quickly achieved under SCF conditions and the product distributions obtained were constant over extended periods of operation (over 40 hours). The SCF-FT process has a marked effect on the hydrocarbon product distribution with a shift to higher carbon number products due to enhanced heat and mass transfer from the catalyst surface. Relatively flat product distributions with similar mass percentages of the C11-C17 products were obtained. In addition, an obvious difference is observed for the 1-olefin content obtained in the SCF-FT synthesis, which is always higher than that from gas or liquid phase FT synthesis. This phenomenon suggests that the SCF-FT reaction rate is not diffusion controlled,

whereas the secondary olefin hydrogenation and isomerization reactions are diffusion limited. The SCF-FT process results in higher diffusivity and more rapid removal of high molecular weight 1-olefins from the catalyst surface thereby suppressing secondary hydrogenation and isomerization reactions.

Catalytic synthesis and testing of oxygenated compounds for use as fuel additives

(Full report – pages 25-41)

Effective catalysts have been developed for the synthesis of several oxygenated compounds that may be useful as fuel additives. These include higher alcohols, higher ethers, and organic carbonates.

- ★ Carbon-supported molybdenum-based catalysts, promoted with Ni and K, were found to be good catalysts for synthesis of higher alcohols from syngas. Reactivity studies were carried out at 250-350°C. The liquid product contained appreciable quantities of C₁₋₅ alcohols in an aqueous phase with no hydrocarbon phase.
- ★ A C₇ ether, 2,3 dimethyl-2-methoxybutane (DM2MB), was synthesized from dimethyl butene and methanol. Several other higher ethers were synthesized from this olefin and butanol, propanol and ethanol, as well as binary mixtures of these alcohols. Reactions were performed using the commercial catalyst, Amberlyst-15, and several laboratory-prepared catalysts ((Zr(SO₄)₂ on sulfuric acid-treated SiO₂).
- ★ Synthesis of diethyl carbonate (DEC) from ethanol, CO, and O₂, was accomplished using a Cu/Pd/activated carbon catalyst pretreated with potassium hydroxide, KOH. X-ray diffraction characterization of the catalysts has established that the most active state of the catalyst is paratacamite, Cu₂Cl(OH)₃.

Diesel engine test facility (Full report - pages 64-66)

A small diesel engine test facility utilizing a two-cylinder Kubota model Z482B has been established. The facility includes a TSI Scanning Mobility Particle Sizer (SMPS) that measures particle size distributions from 7 nm to 300 nm, and a Lasair 310 optical particle counter (OPC) that measures particle counts in seven size ranges from 0.3 μm to 10 μm. The laboratory also has a high volume particulate matter (PM) sampler for collecting large quantities of PM with diameter less than 10 μm. For gas-phase emissions, the laboratory has the capabilities to measure CO, CO₂, NO_x, CO₂ and total hydrocarbons. In addition, the laboratory can measure real-time PAH and elemental carbon on particles. Initial tests conducted using the DEC additive to a conventional diesel fuel exhibited a significant reduction in PM emissions.

Hydrocracking and isomerization of alkane chains representative of FT products

(Full report - pages 13-19)

Laboratory work was then carried out successfully in a small continuous trickle-bed reactor using a Pt/ZrO₂/WO₃ catalyst. A 90 wt% iso-C₁₆ selectivity and a 71wt% iso-C₁₆ yield were achieved at 79 wt% conversion of hexadecane. The objective in the last half-year has been to extend research to the conversion of paraffins longer than hexadecane, such as those produced in the F-T process, to a variety of clean transportation fuels. This was carried out using the stable and selective Pt/ZrO₂/WO₃ catalyst to hydroisomerize and hydrocrack pure compounds, namely n-C₁₆, n-C₂₀, n-C₂₄ n-C₂₈ and their mixtures, representative of alkane chains found in F-T products.

The lube-base oil yield is highest at 79% conversion and consists of only branched isomers, mostly iso-C₂₈. The yield of lube-base oil decreases gradually with increasing conversion as the yield of diesel fuel and gasoline increases. The major product is diesel fuel at 99% conversion, only a 20% change in conversion. If the reaction is carried to 100% conversion, the major product becomes highly branched gasoline. Switching between these three fuels occurs at high conversion values. It appears possible to obtain the desired fuel range by adjusting the conversion at a selected temperature but maintaining relatively high conversion.

Analytical research

Significant progress was made in several areas of analytical research. These results are summarized below.

X-ray diffraction and ESR characterization of Cl catalysts (pages 59-63):

CuCl₂/PdCl₂/activated carbon catalysts are being used for the synthesis of diethyl carbonate (Eyring et al) and Pt/WO_x/ZrO₂ catalysts are being used for the synthesis of high octane-index gasoline components (Wender et al). In our work, we have employed electron spin resonance (ESR) and x-ray diffraction (XRD) to determine the nature of the active species in these reactions, by comparing the catalytic activity with the observed species in XRD and ESR. For Pt/WO_x/ZrO₂, we observe ESR signals, which suggest electron transfer between W⁵⁺ and Zr³⁺ states. For the synthesis of diethyl carbonate, evidence points to paratacamite being the active species. Details of these results will be presented.

Molecular Structure of Binary Methane Decomposition Catalysts (pages 48-51):

Nanoscale, binary Fe-M catalysts supported on alumina (M = Mo, Pd, Ni) exhibit high activity for the catalytic decomposition of methane into hydrogen and carbon nanotubes. In order to better understand the catalytic reaction mechanisms, the molecular structure of the catalysts is being investigated by x-ray absorption fine structure (XAFS) spectroscopy and Mössbauer spectroscopy. Additionally, a high temperature in situ XAFS cell has been constructed to permit investigation of catalyst structure at temperature under reaction conditions. Several conclusions of this work are presented. First, in order for the catalyst to be active, it must be at least partially in the metallic state. This has been confirmed by both in situ XAFS measurements at 700 °C and by ex situ Mossbauer and XAFS measurements at room temperature on previously reduced and reacted catalysts. Second, the spectroscopy data indicates the Mo, Pd, and Ni are all incorporated into an alloy phase with the Fe. In the case of the Mo, a specific intermetallic compound, Fe₂Mo was identified

NMR characterization of particulates from diesel engine tests: The Utah team has focused on two major objectives: 1) synthesis of diethyl carbonate as a fuel additive and 2) obtaining fuel additive performance data in a diesel engine. Synthetic methods have been developed and tested in a batch reactor and a flow reactor. Diethyl carbonate is the primary product in the synthesis scheme but the product distribution seems to vary between the batch and flow reactor processes. ¹³C labeled starting materials

($^{13}\text{CH}_3\text{DH}_2\text{OH}$, $\text{CH}_3^{13}\text{CH}_2\text{OH}$, and ^{13}CO) were used to identify reaction products adsorbed on the catalyst surface and suggest possible reaction pathways for isotope incorporation in the two different processes. NMR and ESR data were obtained on particulate samples collected from diesel engine tests (at idle and under load) of a standard fuel with and without diethyl carbonate additive.