

TECHNICAL PROGRESS REPORT

**For Period Ending 3-31-04
(November 1, 2003 to March 31, 2004)**

Award Number DE-FC26-03NT41964

Sponsor: DOE Pittsburgh Energy Technology Center

**Design, Synthesis, and Mechanistic Evaluation of Iron-Based Catalysis
for Synthesis Gas Conversion to Fuels and Chemicals**

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ABSTRACT

This project explores the extension of previously discovered Fe-based catalysts with unprecedented Fischer-Tropsch synthesis rate, selectivity, and ability to convert hydrogen-poor synthesis gas streams typical of those produced from coal and biomass sources. Contract negotiations between the U.S. Department of Energy and the University of California were completed on December 9, 2004. During this first reporting period, we have modified and certified a previously decommissioned microreactor, ordered and installed a budgeted gas chromatograph, developed and reviewed safe operating procedures and data analysis methods, and reproduced successfully previous synthetic protocols and catalytic performance of catalytic materials based on Fe-Zn-Cu-K oxide precursors synthesized using precipitation methods, drying using surface-active agents, and activated in synthesis gas within Fischer-Tropsch synthesis tubular reactors.

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EXECUTIVE SUMMARY

Fe-based catalysts can be used to convert synthesis gas streams derived from coal and biomass, because their low H_2/CO ratios ($H_2/CO=0.7-1$) can be adjusted by rejecting the excess carbon as CO_2 via concurrent water-gas shift reactions ($H_2O + CO \rightarrow CO_2 + H_2$). In this manner, the stoichiometry required for the synthesis of hydrocarbons useful as fuels and chemicals can be achieved using these H_2 -poor synthesis gas streams. These Fe catalysts are typically much less active than Co-based catalysts, which do not possess water gas shift activity at the temperatures at which they lead to significant hydrocarbon chain growth. In addition, Fe-based catalysts tend to exhibit lower stability as a result of phase transformations and mechanical disintegration, often as a result of their tendency to interconvert between oxide and carbide phases as the redox properties change within Fischer-Tropsch synthesis catalytic reactors. The development of Fe-based catalysts with higher Fischer-Tropsch synthesis (FTS) rates, lower CO_2 selectivity and greater mechanical stability remain the critical hurdles in our ability of convert hydrogen-poor synthesis gas streams, derived from coal and biomass, into high-value fuels and petrochemicals.

This project exploits our recent discovery of catalyst compositions and synthesis and activation protocols that lead to iron-based catalysts with FTS activities and selectivities similar to those on cobalt-based catalyst using stoichiometric H_2/CO streams, while retaining significant water-gas shift activities at the lower temperatures that favor the formation of high molecular weight hydrocarbons and minimize the undesired formation of light alkanes and alkenes. These materials are being tested in this project for the conversion of substoichiometric synthesis gas streams to explore whether the unprecedented activities and selectivities achieved with synthesis gas compositions derived from natural gas can be extended to these more demanding syngas ratios.

During this period, we have started the synthesis of sets of catalytic materials with the intended compositional range. These novel synthesis methods are based on supercritical and subcritical drying of powders after their precipitation as oxides at a constant pH. These methods avoid the pore collapse and loss of surface area that often accompany drying with high surface tension intrapore liquids. These initial results have reproduced our previous findings; surfaces areas have been further improved by extending

the use of surfactants to the impregnation of Cu and K promoters after precipitation of mixed Fe-Zn oxide powders and drying.

During this first reporting period, we were able to contract a post-doctoral fellow within a few weeks of the notification on the part of DOE of their intent to proceed and this post-doctoral fellow arrived on November 1, 2003. The contract negotiations led to a formal approval of a contract by University of California and the Department of Energy on December 9, 2003. Two FeZn oxide precursors were prepared and a high surface area of these precursors was confirmed by physical adsorption methods to be 260 and 270 m²/g, in agreement with earlier synthetic reports. Promotion with K and Cu was achieved by incipient wetness impregnation of these activity and selectivity promoters (Cu, K). A proposal was submitted and approved for beamtime at the Stanford Synchrotron Radiation Laboratory (SSRL) to carry out in situ X-ray absorption spectroscopy (XAS) assessments of the structure and phase transformations of these materials during catalytic Fischer-Tropsch synthesis. This proposal was rated excellent by all three reviewers. Beamtime has been requested for May-August 2004. During this reporting period, we have also reconstructed a previously decommissioned laboratory microreactor. This reactor has been certified for operation up to 50 bar and a safety analysis of operating protocols has been completed. The budgeted gas chromatograph has been installed and tested. One certification run was carried out and previous results were satisfactorily reproduced. Products analysis methods and data reporting procedures were certified and standardized. A detailed experimental plan has been assembled to guide experiments for the next reporting period.

During the next reporting period, we will prepare catalysts with Fe-Zn-Ru-K and a wide compositional range, characterize their structure, and measure their activation dynamics and their steady-state Fischer-Tropsch synthesis rates, selectivity, and stability.

Design, Synthesis, and Mechanistic Evaluation of Iron-Based Catalysis for Synthesis Gas Conversion to Fuels and Chemicals

Objectives and Specific Tasks

Fe-based catalysts are typically preferred in converting coal or biomass derived synthesis gas streams with low H_2/CO ratios ($H_2/CO=0.7-1$) because their significant water-gas shift activity ($H_2O + CO \rightarrow CO_2 + H_2$) leads to rejection of excess carbon as CO_2 . Fe-based catalysts typically show much lower catalytic activities than Co-based catalysts and lower mechanical stability, as a result of their tendency to interconvert between oxide and carbide phases as the redox properties change within catalytic reactors. Fe-based catalysts with higher Fischer-Tropsch synthesis (FTS) activity and greater structural integrity remain significant obstacles to their use in the synthesis of high-value fuels and petrochemicals.

Iron-based catalysts with FTS activities and selectivities similar to those on cobalt-based catalyst using stoichiometric H_2/CO streams derived from natural gas were recently reported by our research group. Novel synthesis methods based on supercritical and subcritical drying of powders after precipitation at a constant pH led to significant improvements in the surface area of oxide precursors, while activation and promotion protocols led to active Fe carbide clusters with high surface areas and mechanical strength. These gave in turn unprecedented activity and C_{5+} selectivity during use with stoichiometric synthesis gas ($H_2/CO=2$).

The principal objectives of this project are to:

1. optimize synthesis protocols to prepare Fe-based catalysts with FTS rates and hydrocarbon product distributions similar to those of Co-based materials using surface-active compounds and supercritical conditions and explore the use of Ru as activation promoter
2. evaluate the performance of prepared catalysts in synthesis gas streams derived from coal or biomass ($H_2/CO = 0.7-1.0$) and optimize activation protocols for high activity, selectivity and mechanical integrity
3. determine the effects of Ru loading and mode of addition on the concentration of active sites and on the intrinsic activity and selectivity of such active sites
4. establish the extent and dynamics of carbide-oxide transformations during reactions of synthesis gas mixtures with varying redox potential and their influence on the structural integrity and stability of Fe-based catalysts

Technical Activities and Accomplishments (FY2004):

1. Post-doctoral fellow Jian Xu arrived at Berkeley on November 01, 2003; an active search for a second post-doctoral fellow is currently underway.
2. Contract formally approved by the University of California and the Department of Energy on December 9, 2003.
3. Two batches of FeZn precursors were prepared using surface-active agents to prevent sintering and maximize surface area during drying. The high surface area of these precursors was confirmed by BET measurements of 260 and 270 m²/g for two separate batches. Three different FeZnKCu catalysts were prepared using these precursors with an aim to optimize catalyst synthesis, specifically the incipient wet impregnation of activating and selectivity promoters (Cu, K).
4. A proposal was submitted to Stanford Synchrotron Radiation Laboratory (SSRL) for in situ X-ray absorption spectroscopic (XAS) studies on December 31, 2003. This proposal was rated excellent by all three reviewers. A beam time request was submitted for the May-August 2004 time period
5. The required microreactor system was refurbished and calibrated. Pressure integrity at 50 bar was confirmed.
6. The installation of the new gas chromatograph was completed on March 19, 2004.
7. A 24-hour microreactor and GC certification run was finished on a newly prepared FeZnK₄Cu₂ catalyst under previous reported FTS conditions (508 K, 2.14 MPa, H₂/CO =2, 3.33 NL/h/g-Fe). The reactor and gas chromatograph performances were certified by comparison with published data at these conditions on catalysts prepared with similar compositions and synthesis protocols. A slightly higher steady state CO conversion was observed (62% vs. 50.8%), while steady state CO₂ selectivity is about the same (32.7% vs. 31.7%). CH₄ selectivity was remarkably low and similar to those reported previously (1.9% vs. 2.0%).
8. FTS product analysis and updated spreadsheet calculation were certified using GC calibrations and GC-MS peak identifications. CO conversion, CO₂, CH₄, C₅+ selectivities and olefin/paraffin ratios (C₅ and C₁₀) were calculated using these calibrations.
9. A detailed experimental plan has been assembled to guide experiments for the next reporting period.

Immediate Next Steps and Research Plan are:

1. Catalyst synthesis: preparation of catalyst precursor with composition: Fe-Zn-K-Ru
2. Determination of physical surface area and reduction properties and comparisons with previous reports; determination of optimum thermal treatment protocols for maximum physical surface area
3. Measurement of activation kinetics in H ₂ -CO mixtures with stoichiometric feeds (H ₂ /CO=2) and determine site density using CO chemisorption protocols. Comparisons with previous data and extend studies and optimize activation for sub-stoichiometric synthesis gas (H ₂ /CO=1)
4. Commencement of catalytic evaluation of materials and thermal treatments in tasks 1-3
5. Design of experimental protocols and choice of materials and specific experiments for X-ray absorption studies