

# **Final Technical Report**

## **NASEO-STAC**

**Project Title: Iron-Based Mixed Metal Carbide Fischer-Tropsch Catalysts**

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**Recipient Organization: Clemson University**

**Partners: Louisiana State University, RTI, Süd-Chemie Inc., Rentech, Energy Technology Partners LLC, the South Carolina State Energy Office, and the Louisiana State Energy Office**

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## PUBLIC ABSTRACT

### "Iron-Based Mixed Metal Carbide Fischer-Tropsch Catalysts"

Research was carried out that addresses the need for highly active, selective, attrition resistant and stable iron-based catalysts for converting low H<sub>2</sub>/CO ratio syngas from coal and biomass to clean fuels, additives, and lubricants using the Fischer-Tropsch synthesis (FTS). The 36-month (plus 16 month no-cost extension) research project involved **Clemson University** (the prime contractor, a state university in South Carolina), **Louisiana State University** (a state university in Louisiana), **RTI** (a non-profit research institution in North Carolina), **Süd-Chemie Inc.** (a private company in Kentucky), **Rentech** (a private company in Colorado), **Energy Technology Partners LLC** (a private company in Pennsylvania), the **South Carolina State Energy Office**, and the **Louisiana State Energy Office**.

Gasification followed by FTS is currently the most promising method for upgrading low-value coal and biomass to high-value liquid fuels and chemicals. There are sufficient domestic reserves of coal to supply most of US fuel needs for more than one hundred years using FTS. Because biomass is formed by fixation of atmospheric CO<sub>2</sub>, its use as a fuel feedstock is attractive because this results in virtually no net CO<sub>2</sub> emissions. The total biomass produced each year as waste material from agriculture and forest operations could be converted into roughly 40 billion gal/yr of liquid fuel, roughly 25% of the current US gasoline usage.

Bulk iron (Fe) catalysts are the catalysts of choice for converting low H<sub>2</sub>/CO ratio syngas to fuels via FTS. These relatively low-cost catalysts have low methane selectivity and high water gas shift activity (which generates H<sub>2</sub> *in situ*). However, development of a bulk Fe FTS catalyst that combines high FT activity, low methane selectivity, high attrition resistance (i.e., ability to withstand physical breakage), and long-term stability (low deactivation rate) is still elusive and presents a widely recognized barrier to the commercial deployment of FTS for coal and biomass conversion. The critical property determining the activity and deactivation of Fe catalysts for FTS appears not to be Fe in the metallic state but the carburized Fe surface.

This research project addressed the issues of the nature, the genesis, and the maintenance of active Fe sites from a totally different perspective than previous studies. Unlike previous studies of Fe bimetallic catalysts, this work focused on the ability of second and third metals to form mixed-metal carbides with Fe at reaction or pretreatment conditions. Improvements in activity resulted as catalytically active surface carbide structures were stabilized in the presence of H<sub>2</sub>O and CO<sub>2</sub>, important for use at the high conversions required for commercial operation. The catalysts synthesized were studied using Fischer-Tropsch synthesis (low pressure gas phase, steady-state isotopic transient kinetic analysis, and high pressure slurry phase using CSTR reactors) and detailed characterization (x-ray absorption fine structure, x-ray diffraction, chemisorption, attrition testing, among others). The results from the various studies compared to benchmark catalysts were used to evaluate commercial potential. The project resulted in the development of two potential commercial Fe-based FTS catalysts having excellent activities, selectivities, and, especially, attrition resistance, the latter very important for any commercial candidate catalyst to be employed in a slurry phase reactor.

## 1.0 STATEMENT OF PROJECT OBJECTIVES

The objective of the research project was to develop more active, selective, attrition resistant and stable Fe FTS catalysts based on formulations containing a second metal (besides Cu) capable of forming mixed metal carbides with Fe. The research addressed the issues of the nature, the genesis, and the maintenance of active Fe sites from essentially a totally different perspective than previous studies. Contrary to previous studies of Fe bimetallic catalysts, this work focused on the ability of the second metal to form mixed-metal carbides with Fe at reaction or pretreatment conditions rather than on the alloying properties of the 2 metals. Improvements in activity were predicted to result as we were able to better stabilize catalytically active surface carbide structures in the presence of H<sub>2</sub>O and CO<sub>2</sub>, important for use at the high conversions required for commercial operation. This was hypothesized to be important also in decreasing the rate of deactivation, thereby improving the longevity of the catalyst. Interesting selectivities, especially low methane production, were expected to possibly result as we modified the nature of the active surface carbide and, potentially, the active sites. The catalysts were initially prepared using methodology developed by members of the team at RTI and Clemson to make them more attrition resistant so that they could be used in slurry phase reaction in an SBCR.

## 2.0 PROJECT ACTIVITIES

Project activities occurred as follows in accordance with the original project schedule with a 16-month no-cost extension.

	Activity																
	Year 1				Year 2				Year 3				NCE Y4				Y5
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1
Task 1: Catalyst Prep.	X	X	X		X		X		X		X			X			
Task 2: Catalyst Charac.	X	X	X	X	X	X	X	X	X	X	X	X	X	X			
Task 3: Reaction Study		X	X	X	X	X	X	X	X	X	X	X	X	X			
Task 4: Slurry Phase Rxtr. Testing			X	X			X	X		X	X			X	X	X	X
Task 5: Eval. of Comm. Potential									X			X			X	X	X

## 3.0 PROJECT PUBLICATIONS AND PRESENTATIONS

### PATENTS:

- [1] James G. Goodwin Jr., Edgar Lotero, Nattaporn Lohitharn, *"Bimetallic Zr-Fe Catalysts for Fischer-Tropsch Synthesis," U.S. Patent Disclosure* (May 15, 2007).

## PEER-REVIEWED PAPERS:

- [1] Kamonchanok Pansanga, Nattaporn Lohitharn, Andrew C. Y. Chien, Edgar Lotero, Joongjai Panpranot, Piyasan Praserttham, and James G. Goodwin, Jr., "Copper-Modified Alumina as a Support for Iron Fischer-Tropsch Synthesis Catalysts," ***Applied Catalysis A:General*** 332 (2007) 130-137.
- [2] A. Campos, J.J. Spivey, A. Roy, N. Lohitharn, J. Goodwin, E. Lotero, and H. Lamb, "Characterization of Mo Additions in Iron-Based Fischer-Tropsch Catalysts using X-ray Absorption Spectroscopy and X-ray Diffraction," ***Nuclear Instruments and Methods in Physics Research, Section A, Accelerators, Spectrometers, Detectors and Associated Equipment*** 582 (2007) 236-238.
- [3] Nattaporn Lohitharn, James G. Goodwin, Jr. and Edgar Lotero, "Fe-Based Fischer-Tropsch Synthesis Catalysts Containing Carbide-Forming Transition Metal Promoters," ***Journal of Catalysis*** 255 (2008) 104-113.
- [4] Nattaporn Lohitharn and James G. Goodwin, Jr., "Impact of Cr, Mn and Zr Addition on Fe Fischer-Tropsch Synthesis Catalysis: Investigation at the Active Site Level using SSITKA," ***Journal of Catalysis*** 257 (2008) 142-151.
- [5] Nattaporn Lohitharn and James G. Goodwin, Jr., "Effect of K Promotion of Fe and FeMn Fischer-Tropsch Synthesis Catalysts: Analysis at the Site Level Using SSITKA," ***Journal of Catalysis*** 260 (2008) 7-16.
- [6] Nattaporn Lohitharn and James G. Goodwin, Jr., "An Investigation using SSITKA of Chain Growth on Fe and FeMnK Fischer-Tropsch Synthesis Catalysts," ***Catalysis Communications*** 10 (2009) 758-762.
- [7] A. Campos, N. Lohitharn, A. Roy, E. Lotero, J.G. Goodwin Jr., J.J. Spivey, "An Activity and XANES Study of Mn-Promoted, Fe-Based Fischer-Tropsch Catalysts," ***Applied Catalysis A:General***, in press (2010).
- [8] A. Campos, S. Vasireddy, N. Lohitharn, A. Roy, J.G. Goodwin Jr., J.J. Spivey, "A Side-By-Side Comparison of Iron Phase Composition and Catalytic Activity for Transition-Metal Promoted Fe-Based Fischer-Tropsch Catalysts," ***Journal of Catalysis***, under review (2010).

## CONFERENCE PRESENTATIONS:

- [1] A. Campos, J.J. Spivey, A. Roy, N. Lohitharn, J.G. Goodwin Jr., E. Lotero and H. Lamb, "Characterization of Mo additions in iron-based Fischer-Tropsch catalysts using X-ray absorption spectroscopy and X-ray diffraction," SRI 2007, Baton Rouge, LA, conference poster (2007).
- [2] Nattaporn Lohitharn, James G. Goodwin, Jr. and Edgar Lotero, "Enhanced Fischer-Tropsch Synthesis Using Transition Metal Modified Bulk Fe Catalysts," 20<sup>th</sup> North American Catalysis Society Meeting, Houston, TX, oral presentation (2007).
- [3] A. Campos, N. Lohitharn, G. Merchan, E. Lotero, A. Roy, J. G. Goodwin Jr., J.J. Spivey, "XANES investigation of Mn-promoted Fe-based Fischer-Tropsch catalysts," 235<sup>th</sup> ACS Meeting, New Orleans, LA, conference presentation (2008).
- [4] A. Campos, N. Lohitharn, G. Merchan, E. Lotero, A. Roy, J. G. Goodwin Jr., J.J. Spivey, "A XANES and XRD study of a Cr-promoted Fe-based FT catalyst," 237<sup>th</sup> ACS Meeting, Salt Lake City, UT, conference presentation (2009).
- [5] A. Campos, N. Lohitharn, A. Roy, J.G. Goodwin Jr., J.J. Spivey, "A TPR XANES and XRD study of transition-metal promoted Fe-based Fischer-Tropsch catalysts," 21<sup>st</sup> North American Catalysis Society Meeting, San Francisco, CA, conference poster (2009).

## 4.0 PROJECT RESULTS

### 4.1 CATALYST DEVELOPMENT

#### 4.1.1 Copper-Modified Alumina as a Support for Iron Fischer-Tropsch Synthesis Catalysts

In this study, the effect of Cu-modified Al<sub>2</sub>O<sub>3</sub> on the properties of Al<sub>2</sub>O<sub>3</sub>-supported Fe catalysts in the Fischer-Tropsch synthesis was investigated. Use of catalyst supports helps to increase the efficiency of the metal catalyst by increasing its surface area/g metal. Alumina or other refractory oxide supported Fe catalysts are, however, usually not very useful due to metal-support compound formation by the base metal Fe. Cu was added to the alumina to try to block the entry points for Fe into the alumina structure by preferentially forming first some form of Cu aluminate. Cu is, in any case, usually added to bulk Fe catalysts to promote reduction of the Fe.

Ten wt% Cu was first impregnated into  $\gamma$ -alumina to produce Cu-modified Al<sub>2</sub>O<sub>3</sub> supports; then 20 wt% of Fe and (in some cases) 1 wt% Cu were added to the supports by the sequential impregnation method. Two different pretreatment methods (drying or drying and calcining) were employed after each metal impregnation.

It was found that the use of Cu-modified Al<sub>2</sub>O<sub>3</sub> supports increased significantly the overall activity of the Fe/Al<sub>2</sub>O<sub>3</sub> catalysts. Incorporation of an additional 1% Cu as a reduction promoter with the Cu-modified supported Fe catalysts was not necessary since it did not further enhance the activity of the catalysts. It was found that the Fe catalysts supported on 10 wt% Cu-modified alumina exhibited significantly higher activities than those of a 1 wt% Cu-promoted Fe/Al<sub>2</sub>O<sub>3</sub> catalyst. There was, however, little effect on FT product selectivity, chain growth probability ( $\alpha$ ), or olefin selectivity. Moreover, calcination after impregnation of each metal during catalyst preparation was important for producing highly active catalysts. It is likely that Cu modification acts to restrict interaction of Fe with the alumina support, known to decrease the activity of Fe for FTS. Use of the Cu-modified support increased both the CO chemisorption and the ease of reduction provided the catalyst was calcined after preparation.

Kamonchanok Pansanga, Nattaporn Lohitharn, Andrew C. Y. Chien, Edgar Lotero, Joongjai Panpranot, Piyasan Prasertdam, and James G. Goodwin, Jr., "Copper-Modified Alumina as a Support for Iron Fischer-Tropsch Synthesis Catalysts," *Applied Catalysis A:General* 332 (2007) 130-137.

#### 4.1.2 Characterization of Mo Additions in Iron-Based Fischer-Tropsch Catalysts using X-ray Absorption Spectroscopy and X-ray Diffraction

Catalysts were synthesized by adding a second metal to iron in order to improve activity, stability, and selectivity due to iron-secondary metal interactions. Characterization of the catalysts using *ex situ* x-ray diffractometry (XRD) and x-ray absorption spectroscopy (XAS) were carried out to provide unique information about the local structures of the central atoms (i.e., Fe, Mo, etc.) that is not possible with other characterization techniques.

An iron-based Fischer-Tropsch (FT) catalysts with a minor amount of molybdenum (90Fe/10Mo/5Cu/17Si) to form mixed metal carbides was prepared using coprecipitation, pretreated in CO, then one sample passivated and one calcined. The XRD data showed that the post-reaction calcined and passivated catalysts were almost x-ray amorphous with respect to  $\text{Fe}_2\text{O}_3$  with nanoparticle sizes of 1Å and  $\text{Fe}_3\text{C}$  in the passivated sample with a particle size of 100Å.

The XANES data using least squares fitting complemented the XRD data showing hematite in the majority of the bulk phase in the calcined 90Fe/10Mo sample as well as in agreement in that  $\theta\text{-Fe}_3\text{C}$  existed in the bulk phase in the passivated 90Fe/10Mo sample. Calcination of the 90Fe/10Mo sample produced a material no difference between the bulk and surface Fe, as expected. Calcination removed any carbide phase from the bulk and surface of the catalyst and even oxidized some carbide precursor magnetite ( $\text{Fe}_3\text{O}_4$ ) to hematite ( $\text{Fe}_2\text{O}_3$ ). The passivated 90Fe/10Mo sample did not form much molybdenum carbide during CO pretreatment. The K and  $L_{III}$  edges Mo XANES showed only a small amount of molybdenum carbide formation compared to iron carbide. No evidence was found for any possible Fe-Mo mixed carbide phase.

A. Campos, J.J. Spivey, A. Roy, N. Lohitharn, J. Goodwin, E. Lotero, and H. Lamb, "Characterization of Mo Additions in Iron-Based Fischer-Tropsch Catalysts using X-ray Absorption Spectroscopy and X-ray Diffraction," ***Nuclear Instruments and Methods in Physics Research, Section A, Accelerators, Spectrometers, Detectors and Associated Equipment*** 582 (2007) 236-238.

#### 4.1.3 Fe-Based Fischer-Tropsch Synthesis Catalysts Containing Carbide-Forming Transition Metal Promoters

Although the impacts of promoters such as K and Cu on the activity of Fe catalysts have been extensively studied, surprisingly, the effects of many other potential promoters for Fe catalysts similar to the commercial Ruhrchemie catalyst have not been significantly investigated or compared directly in a comprehensive study reported in the literature. In this study, the impact of adding variety of different transition metals (Cr, Mn, Mo, Ta, V, W, and Zr) on the catalytic properties of precipitated bulk Fe-based catalysts was investigated using the same preparation method and reaction conditions.

The addition of a third transition metal (Cr, Mo, Mn, Ta, V or Zr) to FeCu-based FTS catalysts increased the catalyst activity for both CO hydrogenation and WGS activity in varying degrees. The addition of W, however, led to lower activity. The dispersion of Fe was enhanced by the addition of all metals studied with the exception of W. Cr, Mn and Zr appear to be the best able to enhance the activity of Fe-based catalysts. WGS activities of these 3 catalysts (FeCr, FeMn and FeZr) were shown to be superior; therefore, they should be able to catalyze FTS under lower  $\text{H}_2/\text{CO}$  ratio syngas derived from biomass or coal.

The high activity observed for the Fe-based catalysts with Cr, Mo, Ta, or V addition was likely due to better Fe dispersions. The high catalytic activities for Mn- and Zr-promoted Fe catalysts, on the other hand, may have been due more to higher intrinsic site activities, as estimated by  $\text{TOF}_{\text{chem}}$  based on CO chemisorption. The selectivities for hydrocarbons and the chain growth probability were not significantly affected, especially at pseudo-steady state, by the addition of any third transition metal.

Nattaporn Lohitharn, James G. Goodwin, Jr. and Edgar Lotero, "Fe-Based Fischer-Tropsch Synthesis Catalysts Containing Carbide-Forming Transition Metal Promoters," *Journal of Catalysis* 255 (2008) 104-113.

#### **4.1.4 Impact of Cr, Mn and Zr Addition on Fe Fischer-Tropsch Synthesis Catalysis: Investigation at the Active Site Level using SSITKA**

Cr, Mn, or Zr promotion of a precipitated Cu-promoted Fe Fischer-Tropsch synthesis (FTS) catalyst significantly improves its catalytic activity. In this study, steady-state isotopic transient kinetic analysis (SSITKA) of methanation was utilized to investigate the activity of these catalysts at the site level allowing a better understanding of how this promotion increases the activity of catalyst.

The activity of the base Fe catalyst was enhanced by promotion with Cr, Mn, and Zr in varying degrees, depending upon the type of added metal and its concentration. The addition of these 3<sup>rd</sup> metals promoted the dispersion of Fe but did not affect significantly either the BET surface area or %reducibility. The activities of the reaction sites (estimated by  $1/\tau_{\text{CH}_4} = \text{TOF}_{\text{ITK}}$ ) were found to be similar, regardless of the type of added 3<sup>rd</sup> metal, suggesting that the active sites for Fe catalysts with or without 3<sup>rd</sup> metal promotion were essentially identical. The higher catalyst activities observed for the Cr, Mn, and Zr-promoted Fe catalysts were found to be primarily the result of an increase in the number of active surface intermediates leading to hydrocarbon product.

Nattaporn Lohitharn and James G. Goodwin, Jr., "Impact of Cr, Mn and Zr Addition on Fe Fischer-Tropsch Synthesis Catalysis: Investigation at the Active Site Level using SSITKA," *Journal of Catalysis* 257 (2008) 142-151.

#### **4.1.5 Effect of K Promotion of Fe and FeMn Fischer-Tropsch Synthesis Catalysts: Analysis at the Site Level Using SSITKA**

Promoting a precipitated FeCuSiO<sub>2</sub> catalyst with Mn has been shown to improve significantly its catalytic activity for the Fischer-Tropsch synthesis (FTS). Although the impact of K promotion on the activity of Fe catalysts with and without Mn addition has been previously studied, no one has previously delineated how K influences the concentration of active surface intermediates and the intrinsic site activities of Fe and, more specifically, Mn-promoted Fe catalysts. This research addressed that issue using steady-state isotopic transient kinetic analysis (SSITKA).

Adding K at relatively low concentrations to the base Fe and Mn-promoted Fe catalysts improved the catalyst activity, but the activity of the catalysts declined with the addition of an excess amount. %Light olefins (C<sub>2</sub>-C<sub>4</sub> fraction) and chain growth probability ( $\alpha$ ) were enhanced as expected with the presence of K, regardless of Mn addition. The addition of K decreased the BET surface area and the concentration of surface exposed Fe<sup>0</sup> atoms (as determined by CO chemisorption). The intrinsic site activities (TOF<sub>ITK</sub>) of all the Fe catalysts determined using SSITKA were essentially identical, regardless of the concentration of added K or Mn promotion. This indicates that adding K to unpromoted or Mn-promoted Fe catalysts did not greatly affect the activity of the active sites. Rather, the higher catalyst activities observed for the Fe and Mn-promoted Fe catalysts with K addition were primarily due to an increase in the number of active surface intermediates leading to hydrocarbon products.

Nattaporn Lohitharn and James G. Goodwin, Jr., "Effect of K Promotion of Fe and FeMn Fischer-Tropsch Synthesis Catalysts: Analysis at the Site Level Using SSITKA," *Journal of Catalysis* 260 (2008) 7-16.

#### 4.1.6 An Investigation using SSITKA of Chain Growth on Fe and FeMnK Fischer-Tropsch Synthesis Catalysts

Although FTS is a simple reaction between CO and H<sub>2</sub>, its reaction mechanism is not straightforward since it involves a large number of surface species for the formation of a variety of products. In this study, steady-state isotopic transient kinetic analysis (SSITKA) was utilized to estimate the average surface residence times leading to CO<sub>2</sub> and various hydrocarbon products in order to investigate chain growth and termination for hydrocarbon products formed on unpromoted and K- and Mn-promoted FeCuSiO<sub>2</sub> catalysts.

The addition of K and Mn to the Fe catalyst promoted significantly the catalytic activity of Fe but did not have a significant impact on the chain growth or chain termination steps. Instead, an increase in the concentration of active surface intermediates leading to hydrocarbon products was the primary cause for the improved catalyst activity. By determining the average surface residence time of the various hydrocarbon products, the estimated reaction times for chain propagation and chain termination steps were estimated. It was found for a H<sub>2</sub>:CO ratio of 20 that chain termination by hydrogenation was relatively faster than chain propagation, which was unaffected by the type of Fe catalyst (with or without promoters).

Nattaporn Lohitharn and James G. Goodwin, Jr., "An Investigation using SSITKA of Chain Growth on Fe and FeMnK Fischer-Tropsch Synthesis Catalysts," *Catalysis Communications* 10 (2009) 758-762.

#### 4.1.7 An Activity and XANES Study of Mn-Promoted, Fe-Based Fischer-Tropsch Catalysts

Iron-based Fischer-Tropsch (FT) catalysts with a mol-based formula of (100-x)Fe/xMn/5Cu/17SiO<sub>2</sub> ( $x \leq 20$ ), were prepared using co-precipitation methods. The calcined catalysts were first activated in H<sub>2</sub> for 12 hours, then reacted in flowing syngas at 1.8 atm, 280°C, and a 2:1 ratio of H<sub>2</sub>:CO. The fresh and reacted catalysts were characterized using X-ray absorption near-edge structure (XANES) to determine changes in the oxidation state and atomic-level environment of the Fe atoms. XANES spectra of the fresh calcined and reacted catalyst were taken using the K edges of Fe (7.112 KeV) and Mn (6.540 KeV) for various Mn metal loadings (x=0, 5, 20).

Mn-promotion of the Fe-based FT catalyst activated in H<sub>2</sub> significantly increased the C<sub>1</sub>-C<sub>8</sub> FTS activity at 1.8 atm, 280°C, 2:1 H<sub>2</sub>:CO ratio. The largest effect was observed from the Mn promoted versus the unpromoted (95Fe5Mn/100Fe) catalyst. Subsequent increases in the Mn concentration (80Fe20Mn/95Fe5Mn) had far less effect on activity.

The least squares fitting of the reacted catalyst showed that higher Mn loadings led to decreased  $\theta$ -Fe<sub>3</sub>C concentration and increased Fe<sub>3</sub>O<sub>4</sub> concentration. Principal Component Analysis (PCA) of Fe indicates that the Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>,  $\theta$ -Fe<sub>3</sub>C phases were present, in either the calcined or reacted catalyst. One additional Fe-containing phase was present in the catalyst but was not able to be identified using the Fe standards. The PCA of Mn showed the presence of

Mn<sub>2</sub>O<sub>3</sub>, as well as one additional Mn-containing phase. The average oxidation state of Mn in the 95Fe5Mn catalyst after reaction was  $2.24 \pm 0.07$ , consistent with the formation of an additional phase, identified as (Fe<sub>1-y</sub>Mn<sub>y</sub>)<sub>3</sub>O<sub>4</sub>. The Mn XANES of the reacted 95Fe5Mn and 80Fe20Mn catalysts show that Mn was a mixture of the 2+ and 3+ oxidation states. FEFF calculations have shown relatively good agreement for Mn-substitution of octahedral Fe sites in Fe<sub>3</sub>O<sub>4</sub> (28664-ICSD), specifically in the pre-edge region; corresponding to the composition of (Fe<sub>1-y</sub>Mn<sub>y</sub>)<sub>3</sub>O<sub>4</sub>.

The mixed metal oxide is believed to decrease the reducibility of iron through a stabilization of the Fe<sub>3</sub>O<sub>4</sub> phase [reducibility: (Fe<sub>1-y</sub>Mn<sub>y</sub>)<sub>3</sub>O<sub>4</sub> < Fe<sub>3</sub>O<sub>4</sub>], which is a precursor for  $\theta$ -Fe<sub>3</sub>C [37, 49]. While  $\theta$ -Fe<sub>3</sub>C (or more generically, Fe<sub>x</sub>C) is widely accepted as the active phase in Fe-based FTS, Mn-promotion decreases the concentration of this phase. Iron-based catalysts are thought to deactivate due to inert carbon deposition on the surface of larger iron carbide clusters. The results here suggest that Mn limits the crystallization of  $\theta$ -Fe<sub>3</sub>C, which limits graphitic deposits on the catalyst. Therefore, it would appear that Mn promotion leads to the observed increases in FT activity by decreasing the reducibility of the iron carbide precursor [reducibility: (Fe<sub>1-y</sub>Mn<sub>y</sub>)<sub>3</sub>O<sub>4</sub> < Fe<sub>3</sub>O<sub>4</sub>] and limiting  $\theta$ -Fe<sub>3</sub>C crystallization.

A. Campos, N. Lohitharn, A. Roy, E. Lotero, J.G. Goodwin Jr., J.J. Spivey, "An Activity and XANES Study of Mn-Promoted, Fe-Based Fischer-Tropsch Catalysts," *Applied Catalysis A: General*, in press (2010).

#### 4.1.8 A Side-By-Side Comparison of Iron Phase Composition and Catalytic Activity for Transition-Metal Promoted Fe-Based Fischer-Tropsch Catalysts

This study focused on third transition metal promoted iron-based Fischer-Tropsch catalysts (with a similar formulation to the industrial Ruhrchemie catalyst otherwise) having a mol.-based formula of 95Fe/5Me/5Cu/17SiO<sub>2</sub> (Me = Cr, Mn, Mo, W, Zr). 100Fe/5Cu/17SiO<sub>2</sub>, as well as an Fe<sub>2</sub>O<sub>3</sub> std., were also studied for comparison. The study made use of in situ TPR Fe K-edge XANES in syngas, XRD, and RGA via mass spectrometry. The XANES and RGA characterization techniques correlated bulk phase changes with the WGS and FTS activity.

Based on the TPR XANES data, it appears that Cu and Si have complementary roles in the reduction of the Fe-based catalyst. Since Cu reduces at a lower temperature relative to Fe, it appears that the role of Cu is to increase the reducibility of Fe to lower oxidation state oxides. SiO<sub>2</sub> appears to stabilize the 2+ oxidation state and suppress the formation of Fe<sub>x</sub>C; in fact, two Fe<sup>2+</sup>-containing phases were observed in the bulk: Fe<sub>2</sub>SiO<sub>4</sub> and FeO. The XANES data suggests that the FeO phase is the precursor for Fe<sub>x</sub>C and that the Fe<sub>2</sub>SiO<sub>4</sub> phase suppresses the formation of Fe<sub>x</sub>C; therefore suggesting chemical interactions between the FeO and Fe<sub>2</sub>SiO<sub>4</sub> phases. The role of Si and Cu are clear when comparing the phase composition of the Cu and Si promoted catalyst to the Fe<sub>2</sub>O<sub>3</sub> std., which did not form any observable Fe<sup>2+</sup> phase in the bulk, yet it formed the greatest amount of Fe<sub>x</sub>C.

The RGA suggested that CO reduced Cu, since the 'low temperature' CO<sub>2</sub> peak was observable before the reduction of Fe. The 'low temperature' H<sub>2</sub>O peak corresponded to the reduction of Fe, which was believed to be from the Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> → FeO transition, was due to the complementary roles of Cu and Si. The Fe<sub>2</sub>O<sub>3</sub> std. did not have either a CO<sub>2</sub> or H<sub>2</sub>O 'low temperature' peak; in addition, the Fe<sub>2</sub>O<sub>3</sub> std. directly reduced to the Fe<sub>x</sub>C phase, with no stable Fe<sup>2+</sup> intermediate, further demonstrating the important role of Cu to increase the reducibility and Si to stabilize the Fe<sup>2+</sup>-containing phase.

The RGA also has shown observable formation of CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub> (and higher HCs) approximately 25-50°C after the onset of the Fe<sub>x</sub>C phase observed in the bulk. While the shape of the CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> peaks are similar, there is a slight shift to the right (~20°C) between the CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> at the onset of hydrocarbon formation. This implies:

- Fe<sub>x</sub>C is the active phase for hydrocarbon formation
- Surface Fe<sub>x</sub>C contributed to FT activity, but was more active for methanation
- Bulk Fe<sub>x</sub>C contributed to FT activity, and was more active for formation of higher HCs

The effect of the transition metals W, Mo, Cr appears to be as a chemical promoter which alters the affinity for FeO and SiO<sub>2</sub>. Mo appears to decrease the FeO and SiO<sub>2</sub> affinity, whereas Cr and W increase it. This work suggests Fe<sub>2</sub>SiO<sub>4</sub> limits the formation of the Fe<sub>x</sub>C phase; therefore by controlling the affinity of Fe and SiO<sub>2</sub> affects the formation of the Fe<sub>x</sub>C phase.

The Zr and Mn-containing catalysts deviated from the trend line for Fe<sub>x</sub>C amount formed versus that of Fe<sub>2</sub>SiO<sub>4</sub>, which fit well for the other catalysts that were tested (95Fe5Cr, 100Fe, Fe<sub>2</sub>O<sub>3</sub> std., 95Fe5Mn, 95Fe5W). This suggests that the Mn and Zr promotion effects are stronger than chemical promotion. Since neither Mn nor Zr reduces to the metallic oxidation state until well after the temperatures of interest in this study, suggests that a mixed metal oxide formed, which significantly changed the bulk chemistry of Fe. Despite the relatively low promotion levels (mol ratio: Fe:Me = 19:1), Lohitharn et al. has found a significant improvement for the initial and steady-state activities for CO hydrogenation (C<sub>1</sub>-C<sub>8</sub>) and WGS, especially for the Mn and Zr-containing catalysts; the mixed metal oxide formation significantly altered the bulk chemistry of Fe, which is consistent with those findings.

A. Campos, S. Vasireddy, N. Lohitharn, A. Roy, J.G. Goodwin Jr., J.J. Spivey, "A Side-By-Side Comparison of Iron Phase Composition and Catalytic Activity for Transition-Metal Promoted Fe-Based Fischer-Tropsch Catalysts," *Journal of Catalysis*, under review (2010).

## 4.2 EVALUATION OF COMMERCIAL POTENTIAL:

### 4.2.1 Catalysts and Experimental Procedures

Iron-based catalysts formulated by Clemson University, shown in laboratory studies at Clemson University to offer commercial potential as Fischer-Tropsch synthesis catalysts, and prepared in larger batches using accepted industrial preparation procedures by Rentech were studied under typical commercial reaction conditions in Continuous Stirred Tank Reactors (CSTR).

Five separate CSTR runs were carried out by Energy Technology Partners, LLC of the catalysts prepared by Rentech according to the formulations supplied by Clemson University, as well as two tests with a reference catalyst ( REF Cat) supplied by Rentech. The compositions of the final catalysts in the calcined state are shown in Table 1. The composition of the reference catalyst was unknown, except that it contained 66.7 wt% iron and represented a reasonable comparison to other existing commercial Fe-based FTS catalysts. FeMnK-2 represents a second preparation of a catalyst with the same composition as FeMnK which was tested at the end of this project to test different activation conditions.

**Table 1. Catalyst Composition**

Composition/wt%	FeK	FeMnK and FeMnK-2	FeZrK
Fe <sub>2</sub> O <sub>3</sub>	82.10	71.21	70.53
MnO <sub>2</sub>	0.00	10.83	0.00
ZrO <sub>2</sub>	0.00	0.00	12.15
CuO	4.10	4.50	3.88
K <sub>2</sub> CO <sub>3</sub>	2.80	2.46	2.44
SiO <sub>2</sub>	11.00	11.00	11.00

Prior to loading them into the reactors, the catalysts were all pre-sieved to remove fines with particle size less than 25 µm in order to avoid filter plugging. The weight of samples of various particle size distribution obtained after sieving the catalysts supplied by Rentech is shown in Table 2.

**Table 2. Catalyst Weights / Particle Size Distribution**

	> 25 µm (500 mesh)	Fines < 25 µm
FeK	22.8 g	40.9 g
FeZrK	24.6 g	35.1 g
FeMnK	37.3 g	37.4 g
FeMnK-2	50.2 g	8.0 g

First, the tests with the three catalysts FeK, FeMnK, and FeZrK were carried out according to the following protocol:

1. The reactors (½ liter CSTRs) were filled with adequate amount of start-up liquid and 20g of catalyst
2. The mixing rate was set to 750 rpm.
3. The reactors were flushed with N<sub>2</sub> and leak tested.

4. The reactors were pressurized to 30 psig in N<sub>2</sub>.
5. The reactors were heated up to 180°C under 30 psig of N<sub>2</sub>.
6. Once the temperature reached 180°C, the N<sub>2</sub> was replaced with a mixture of H<sub>2</sub> and CO (H<sub>2</sub>/CO= 1.3) at a space velocity of 2.73 nl/g Fe/h and the temperature was ramped to 280°C at the rate of 5°C /min.
7. At the end of the ramp, the temperature was held at 280°C for 12 h.
8. At the end of the activation period, the reactors were cooled to 255°C, and pressurized to 375 psig. The composition of the feed gas was changed to 97% syngas (H<sub>2</sub>/CO:1.0) and 3% N<sub>2</sub>.
9. The syngas flow was changed to provide a space velocity of 3.7 nl/g Fe/h.
10. On-line exit gas analyses were carried out at regular intervals in order to assess the catalyst performance. The liquid production was measured every other day by weighing the collected reactor effluent. Material balances and other appropriate calculations were monitored periodically for confirmation that the runs are providing the desired results. Conversion, total hydrocarbon production rates as well as C5+ rate, selectivities were calculated after each tail gas analysis.

The catalyst FeMnK was rerun using the same protocol as described above except for the activation temperature and H<sub>2</sub>/CO ratio which were decreased from to 280 to 270°C and from 1.4 to 1.0, respectively. The reaction conditions were kept the same as those used in the first run.

For the reference catalyst (REF Cat), slightly different activation and reaction conditions were provided by Rentech. The following conditions were used:

Activation: 275°C, 140 psig, 6 h hold, H<sub>2</sub>/CO=1.4, 10% N<sub>2</sub>, Space velocity: 2.5 nl/g Fe/h

Reaction: 255°C, 375 psig, H<sub>2</sub>/CO=0.77, 10% N<sub>2</sub>, Space velocity: 3.45 nl/g Fe/h

For FeMnK-2, the following activation conditions were used: **285°C for 24 h** (instead of 12 h), **1 atm** (instead of 30 psi), H<sub>2</sub>/CO= 1.3, a space velocity of **2.0 nl/g cat/h** (instead of 2.73 nl/g Fe/h). The reaction conditions were the same as described in the above protocol.

#### 4.2.2 Results and Discussion

The tests with the first three catalysts formulated by Clemson University were run for approximately 6.5 days, except for the FeMnK catalyst which had to be stopped after 4 days because of a mechanical problem (stirrer malfunction). Figures 1-3 show the data (CO Conversion, Activity and Selectivities for CO<sub>2</sub> and C5+) obtained during these first three runs.

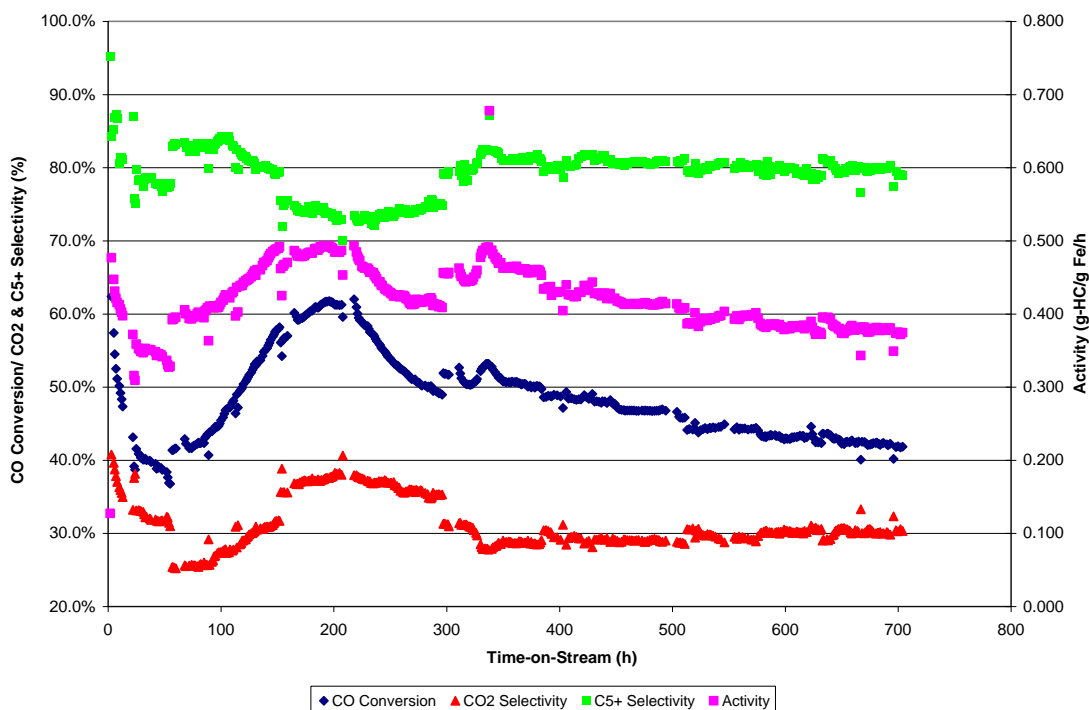
An analysis of the data at this stage (see Figure 4 showing the activity of all the catalysts tested for a period of 5-6 days) showed that the FeK catalyst had the highest activity. All three catalysts showed a sharp decline in activity during the first 24 h under reaction conditions. After

the first day, the zirconium promoted catalyst FeZrK reached a relatively stable activity for the remaining 5 days. However, its activity was the lowest compared to the other two catalysts.

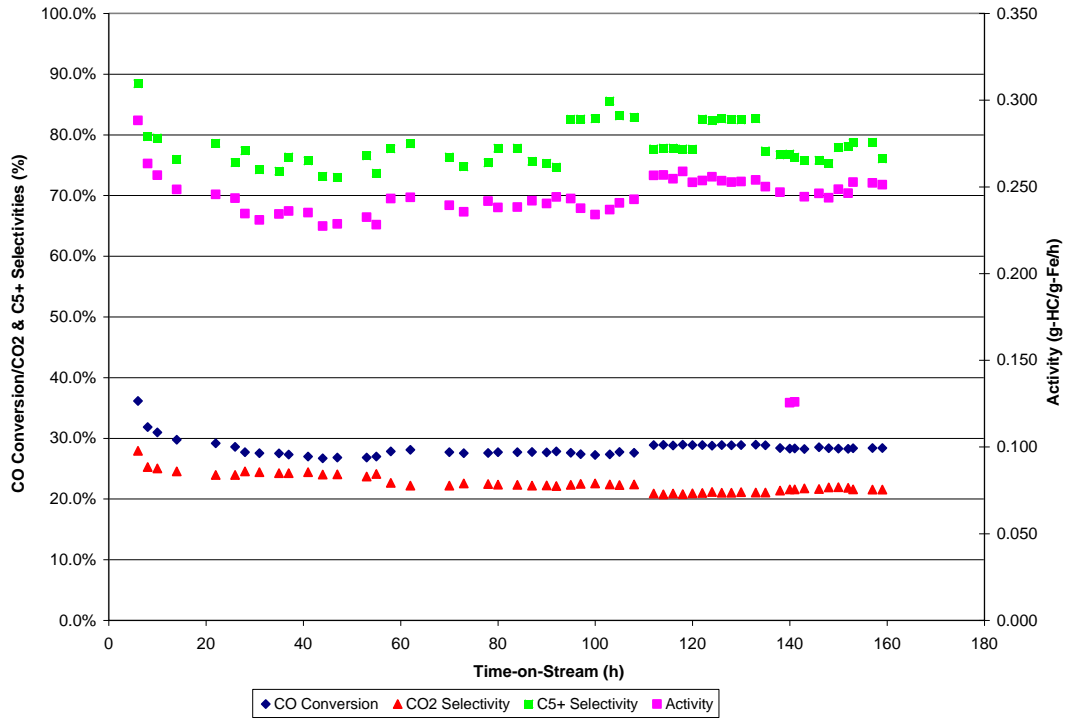
The manganese promoted catalyst FeMnK and the base catalyst FeK experienced a different behavior. After the first 24 hr activity decline and somewhat leveling off for about 30 h the activity of FeMnK which was at about the same level as that of the FeZrK started to increase during the following 2 days-on-stream. At about 100 hours-on-stream, the operation of the stirrer started to be erratic. All attempts to solve the problem were unsuccessful and the run had to be terminated to make the necessary repairs.

The base catalyst FeK which started with the highest activity had the same behavior as the catalyst FeMnK, i.e., initial decline of the activity in the first day followed by leveling off and continuous increase in activity for the following 3 days. Since this catalyst showed the best performance after five days-on-stream it was decided to continue this test for a total period of up to 30 days or until it starts showing significant deactivation. This catalyst reached its highest activity of 0.515 g-HC/g-Fe/h after six days-on-stream. The activity stabilized at this level for another three days-on-stream. Then, a sharp decline in activity for about one day-on-stream was followed by a day of leveling off before another increase in activity, returning on the 14<sup>th</sup> day-on stream to the highest value recorded after six days-on-stream. This increase in activity was followed by seven days-on-stream of a much slower deactivation rate before it reached an activity of about 0.400 g-HC/g-Fe/h which was maintained for the following nine days-on-stream. This strange behavior observed for both the manganese promoted catalyst FeMnK and the base catalyst FeK could be attributed to inappropriate activation conditions which did not result in a complete carbiding of the catalysts.

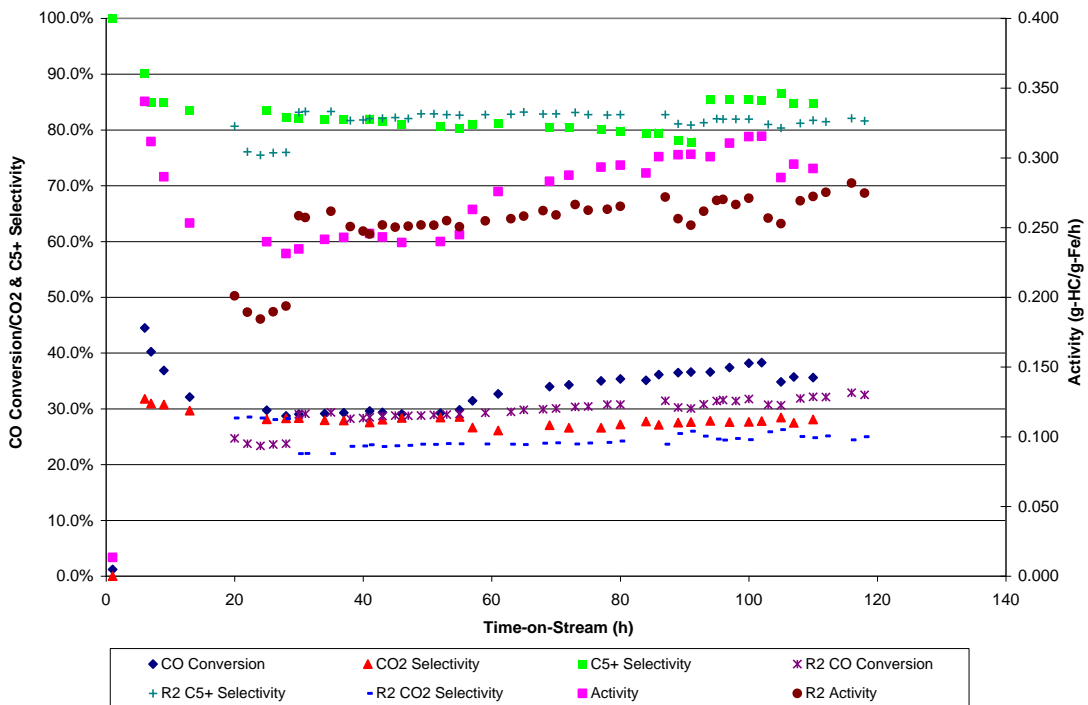
**Figure 1: FeK - CO Conversion/Activity/CO<sub>2</sub> & C<sub>5</sub>+ Selectivity**



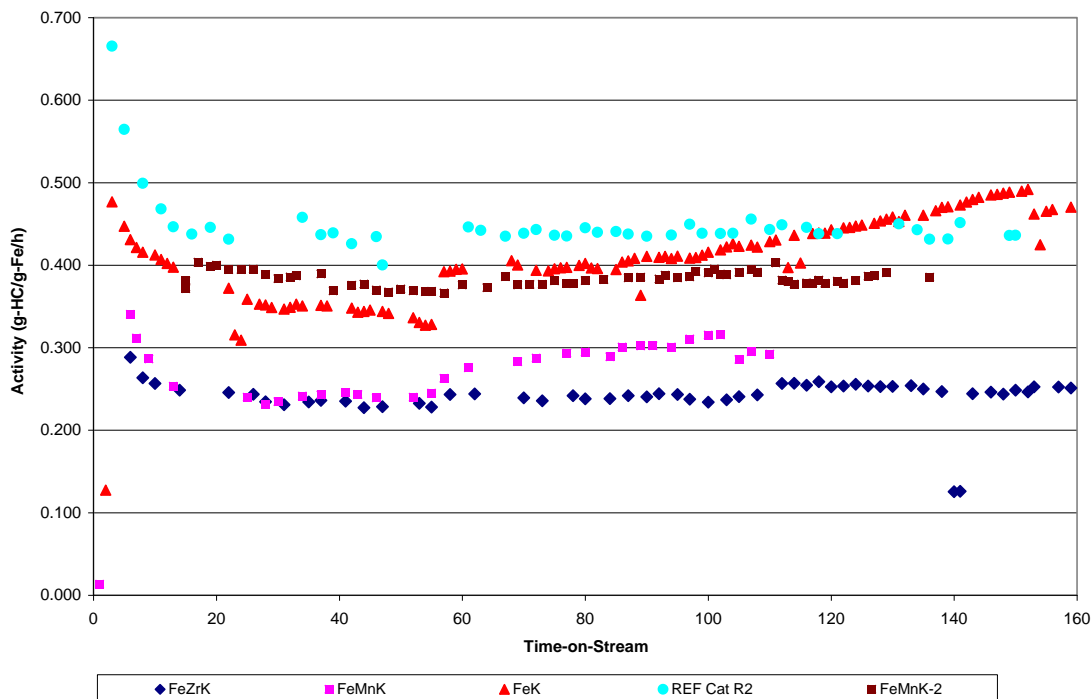
**Figure 2: FeZrK - CO conversion/Activity/CO2 & C5+ Selectivity**



**Figure 3: FeMnK - CO Conversion/Activity/CO2 & C5+ Selectivity (Run 1 & 2)**



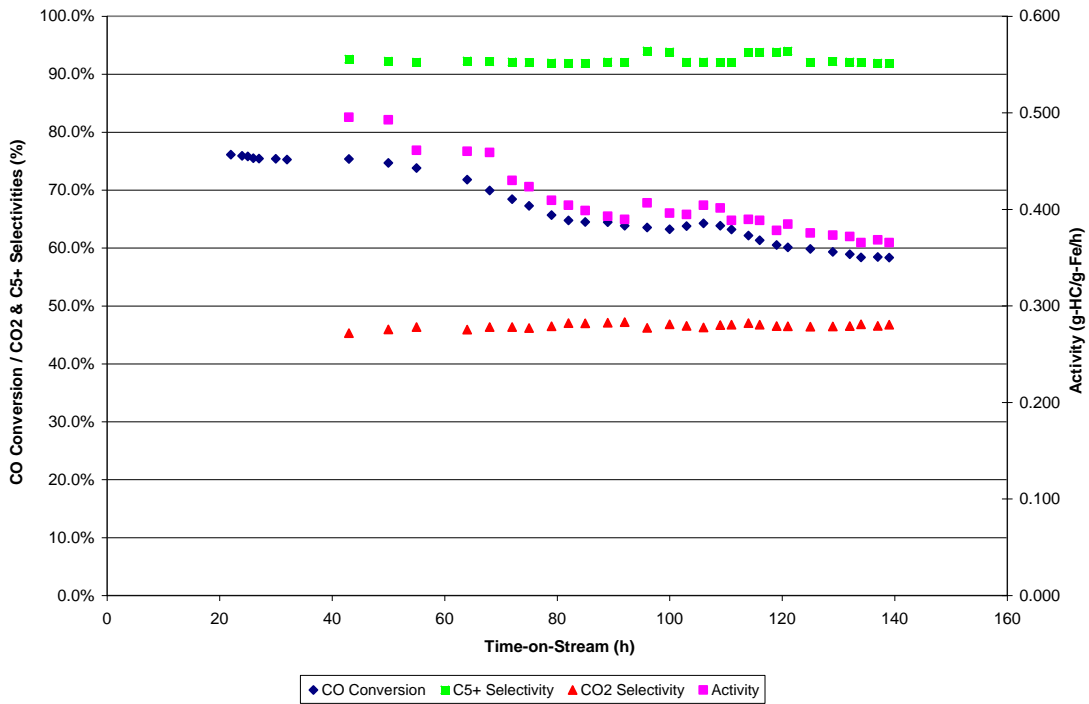
**Figure 4: Fe Catalysts Activity Comparison**



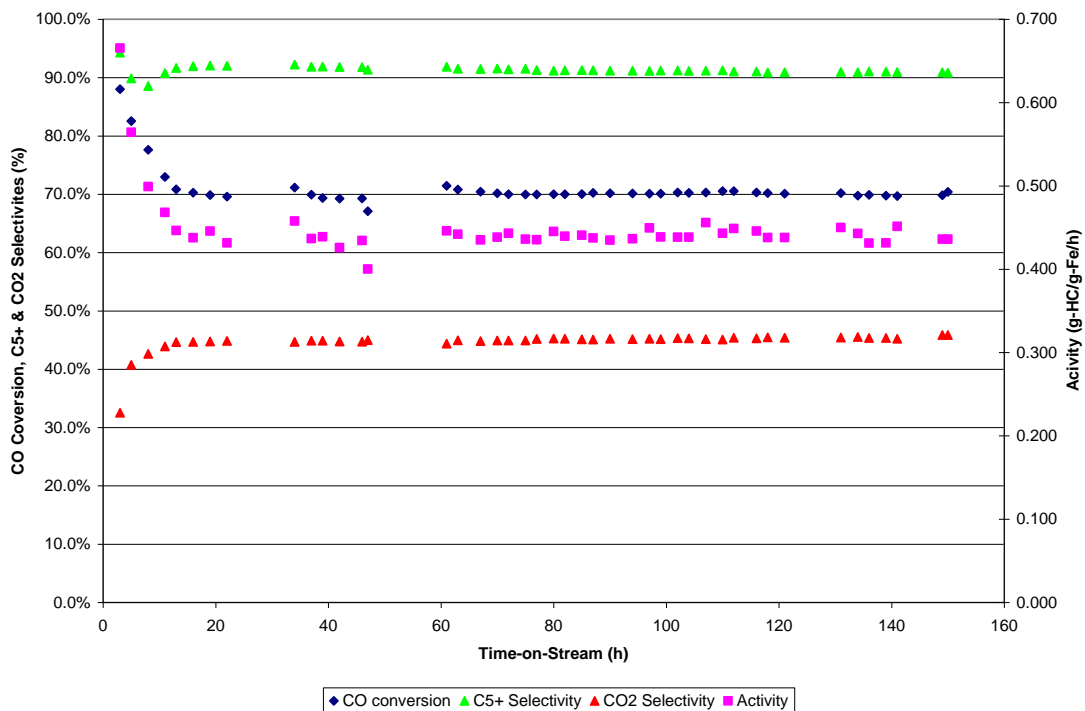
The reference catalyst supplied by Rentech (labeled REF Cat), which had been previously tested in a CSTR at Rentech, was loaded in one of the CSTR systems at the end of the three previous tests to validate as much as possible the results obtained from the three catalysts. As shown in Figure 5 (CO Conversion, Activity and Selectivities for CO<sub>2</sub> and C5+ obtained for REF Cat), the reaction started with high CO conversion. However, after about 50 hours-on-stream the activity started to drop very quickly. The decline continued till the run was stopped at 139 hours-on-stream because of filter plugging and wax and catalyst being pushed overhead to the hot separator. So, the major decline was most probably due to loss of catalyst during the period starting at about the 50 hour point. Due to some problems with the CO<sub>2</sub> analysis in the earlier part of the run, we have only 2 or 3 data point for this period. So it was decided to rerun this test with some minor changes in the hardware to overcome some of the problems, most probably due to excessive attrition, encountered in the first run.

As illustrated in Figure 6, the second run with the reference catalyst showed a much more stable behavior after the initial drop in activity during the first 24 hours-on-stream. For the following four days-on-stream the catalyst activity leveled off at about 0.435 g-HC/g-Fe/h. This activity was higher than that of the Zr- and Mn-promoted catalysts, but lower than the FeK catalyst during the same period (See Figure 4).

**Figure 5: REF Catalyst - CO Conversion / Activity/ CO2 & C5+ Selectivity**



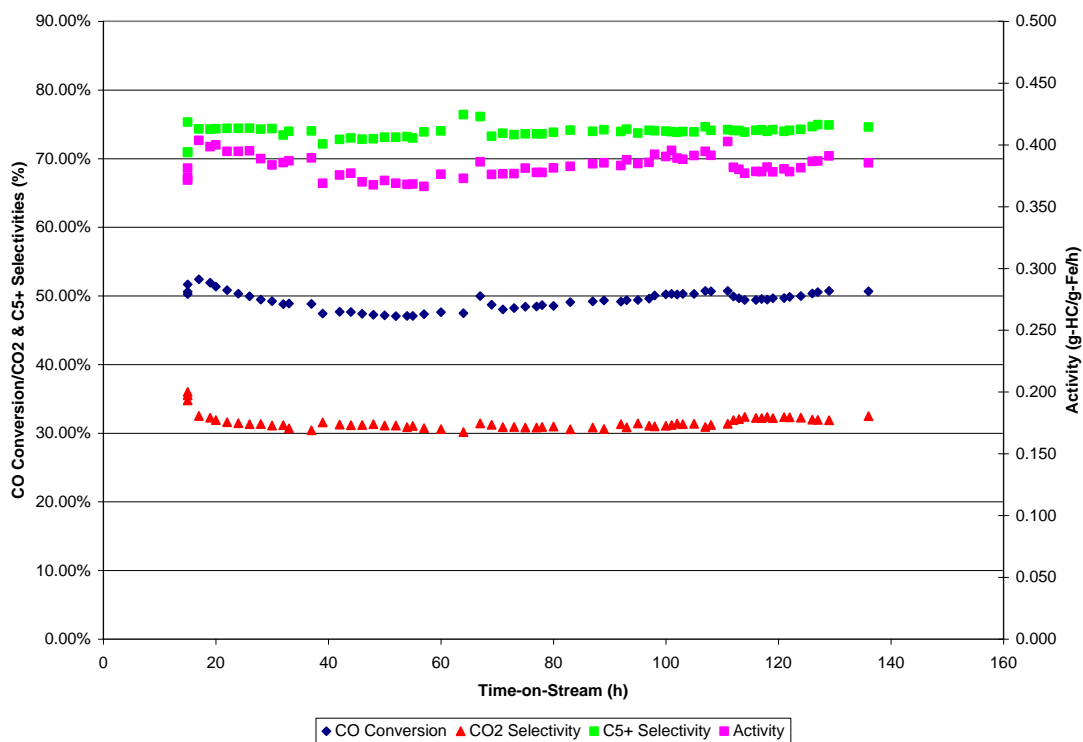
**Figure 6: REF Catalyst: CO Conversion / Activity / C5+ & CO2 Selectivities (Run 2)**



The Mn-promoted catalyst, FeMnK, was retested in the CSTR for a period of 5 days to check that the results obtained in the first run are reproducible. The results are shown in Figure 3 with the corresponding results of the first run. Despite some variation between 60 and 105 hours-on-stream, the catalyst activities and selectivities recorded for both runs outside this period were almost identical.

A second batch of the Mn-promoted catalyst, FeMnK-2 was prepared by Rentech in order to test a new set of activation conditions, especially longer time of activation. The catalyst was run in a CSTR for 5 days with the new activation conditions and the results are shown in Figure 7. The catalyst activity was lined up after only 15 hours-on-stream and remained stable for the following 5 days. With an increase from 275 to 382 g-HC/g Fe/h at 118 hours-on-stream (end of run for the first batch), the activity of this second batch was almost 40% higher than that of the first batch. These results showed a need to optimize the activation conditions.

**Figure7: FeMnK-2 - CO Conversion/Activity/ CO2 & C5+ Selectivity**



The liquid products and wax collected at the end of the run (after 30 days-on-stream) for the FeK test were analyzed and the results are shown as alcohol in water (Table 3), alcohols, olefins and paraffin in the liquid products (Table 4). The wax was analyzed to determine the

Anderson-Shulz-Flory chain growth probability,  $\alpha$ . The  $\alpha$  value estimated in the carbon range of C17-C92 was 0.92.

**Table 3. Water analysis**

<b>Alcohols in Water</b>	
<b>Analyte</b>	<b>Weight %</b>
Methanol	1.39%
Ethanol	2.83%
1-Propanol	1.11%
1-Butanol	0.32%
Pentanol	0.14%
1-Hexanol	0.02%
1-Heptanol	0.00%
1-Octanol	0.00%
1-Nonanol	0.00%
Decyl Alcohol	0.00%
<b>Total Alcohols</b>	<b>5.82%</b>

**Table 4. Liquid hydrocarbon analysis**

<b>Alcohols in Oil</b>	
<b>Analyte</b>	<b>Weight %</b>
Methanol	0.110
Ethanol	0.441
Propanol	0.762
Butanol	1.577
Pentanol	2.039
Hexanol	1.948
Heptanol	1.893
Octanol	1.394
Nonanol	1.070
Decanol	1.030
Undecanol	0.427
Dodecanol	0.498
Tridecanol	0.282
Tetradecanol	0.132
Pentadecanol	0.073
Hexadecanol	0.076
Heptadecanol	0.040
Octadecanol	0.023
Nonadecanol	0.015

<b>Olefins in Oil</b>	
<b>Analyte</b>	<b>Weight %</b>
1-Butene	0.180
1-Pentene	1.202
1-Hexene	3.148
1-Heptene	4.647
1-Octene	4.758
1-Nonene	4.229
1-Decene	3.436
1-Undecene	2.663
1-Dodecene	1.902
1-Tridecene	1.305
1-Tetradecene	0.791
1-Pentadecene	0.505
1-Hexadecene	0.328
1-Heptadecene	0.265
1-Octadecene	0.124
1-Nonadecene	0.088
C20=	0.043
C21=	0.023
C22=	0.022
C23=	0.004

<b>Paraffins in Oil</b>	
<b>Analyte</b>	<b>Weight %</b>
Butane	0.081
Pentane	0.513
Hexane	1.329
Heptane	2.050
Octane	2.683
Nonane	2.713
Decane	2.793
Undecane	2.773
Dodecane	2.793
Tridecane	2.841
Tetradecane	2.753
Pentadecane	2.483
Hexadecane	1.970
Heptadecane	1.405
Octadecane	0.938
Nonadecane	0.579
C20	0.343
C21	0.203
C22	0.125
C23	0.068
C24	0.041
C25	0.025
C26	0.015

Measurements of the particle size distribution of all the fresh and used catalysts were carried out by Rentech using a Horiba instrument in order to determine the extent of attrition during the CSTR tests. The fresh catalysts were all screened through a 500 mesh sieve and had less than 1% fines smaller than 10  $\mu\text{m}$ .

**Table 5. Particle size distribution of the fresh and used catalysts.**

Catalysts	Horiba								
	Average, micron	d50, micron	d10, micron	d90, micron	>100 micron, %	>50 micron, %	<40 micron, %	<20 micron, %	<10 micron, %
FeK	38.8	37.0	26.5	53.5	0.0	11.9	58.9	1.2	0.0
FeK (used- 30 day-run)	35.2	33.9	23.5	48.7	0.0	6.6	71.1	3.8	0.0
FeMnK	53.6	50.0	29.8	82.1	3.3	46.9	26.3	2.6	0.3
FeMnK	48.2	45.6	29.1	71.4	0.8	36.1	32.9	1.5	0.0
FeMnK (used - 4 day-run)	10.6	9.4	4.9	17.8	0.0	0.0	99.8	93.3	55.3
FeMnK (used -5 days on stream-2nd run)	42.2	40.7	17.9	67.4	0.7	28.3	46.5	12.1	3.4
FeZrK	48.5	45.6	29.2	72.5	1.1	36.3	32.9	1.6	0.0
FeZrK (used - 6 day-run)	40.7	40.2	15.3	63.6	0.5	24.1	47.1	12.9	6.6
RefCat	85.8	82.8	51.1	126.7	25.5	89.8	4.8	2.8	1.6
RefCat (Used-Run 1)	26.5	19.3	6.9	56.2	0.5	12.9	76.4	51.3	22.3
RefCat (Used-Run 1- Recovered in Overhead liquid)	4.9	3.5	1.1	10.4	0	0	100	98.8	89.4
RefCat used-Run 1- Recovered in Wax)	28.2	24.7	9.0	52.1	0.1	10.4	75.5	40.2	13.1
RefCat (Used-Run 2)	25.2	23.5	6.7	45.7	0.0	5.5	81.9	42.1	18.6

The catalyst FeK was the most stable of all 4 catalysts even after 30 days-on-stream, with the average particle size dropping from 38.8 to 35.2  $\mu\text{m}$  and 0% fines less than 10  $\mu\text{m}$ . However, since the used catalyst recovery was not done under the same conditions as for the other catalysts, it may be assumed that some agglomeration may have occurred during the carbon burn off.

The catalyst FeZrK was relatively stable but showed some attrition after 6 days with the average particle size dropping from 48.5 to 40.7  $\mu\text{m}$  and with 6% fines less than 10  $\mu\text{m}$ .

The FeMnK used in the first run which encountered some stirrer problems had the lowest attrition resistance of the three Clemson University catalysts. However, the same catalyst recovered from the second run after 5 days-on-stream showed a similar behavior to the catalyst FeZrK, with the average particle size dropping from 48.2 to 42.2  $\mu\text{m}$  and with only 3.4% fines less than 10  $\mu\text{m}$ .

The Rentech Reference catalyst in both runs had a very poor attrition resistance compared to the other 3 catalysts. Its average particle size dropped from 85.8 to 26.5  $\mu\text{m}$  and 28.2  $\mu\text{m}$  for the first and second run, respectively, and with only 22.3% and 18.6% fines less than 10  $\mu\text{m}$ . Some fines were carried overhead with the product vapors, probably due to foaming in the reactor, and were recovered from the liquid products.

### **4.2.3 Additional Work Planned using Rentech Facilities**

The high attrition resistance of the Mn- and the Zr-promoted catalysts formulated by Clemson University as compared to the Rentech catalyst, at least for the first five days-on-stream, offers a significant advantage despite their somewhat lower activity which, as seen with the test of the catalyst FeMnK-2, can be improved by optimizing the activation conditions. Thus, it is now important to confirm both this improved attrition resistance over a longer period of run time and at the same time check for overall stability of the catalyst and its reaction properties. Because of scheduling issues with our industrial partners and the presence of the economic recession that resulted in some of the scheduling delays, not all the originally planned activities were able to be accomplished in the time allotted. However, the results to date has suggested that at least one stable and active catalyst that would be suitable for commercial production of hydrocarbons has been developed. Thus, even though the NASEO-funded portion of this project reached its termination date on December 31, 2009, it has been decided that Rentech will prepare in the first quarter of 2010 a new batch of the FeMnK catalyst and will run a longevity test of 500 to 3000 hours in a CSTR at Rentech, as part of their cost sharing of this project. The run will be carried out until it starts showing significant deactivation. This work is currently underway at Rentech.

## **5.0 SUMMARY**

The activities of this project have resulted in the development of at least one and possibly two catalysts that are as good or better in overall ability than other potential commercial Fe-based catalysts for the Fischer-Tropsch synthesis of hydrocarbons (liquid fuels and chemicals) from syngas ( $\text{CO} + \text{H}_2$ ) prepared from coal, biomass, or natural gas. These catalysts exhibited excellent activities and selectivities, but, perhaps even more importantly, outstanding attrition resistance which can permit them to be used in preferred slurry phase reactors. Even though this project has now reached its termination date, Clemson University will continue in 2010 to collaborate with Energy Technology Partners LLC and Clemson's cost-share partner Rentech to carry out additional long term (500-3000 h) slurry phase runs with at least the FeMnK catalyst.