

## **(22) Iron-Based Mixed Metal Carbide Fischer-Tropsch Catalysts**

This three-year effort will seek to develop a 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.

Total project cost: \$1,334,594

Funding request: \$875,499

Project Lead: Clemson University

Project Participants: Louisiana State University; RTI; Rentech; Sud-Chemie, Inc.; South Carolina Energy Office; Louisiana State Energy Office

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End Date: August 31, 2008

### Presentations/Publications

None.

### Patents

None.

### Progress in Past Quarter and Current Status

Project activities are progressing in accordance with the project schedule. During this third quarter of activities the main focus has been placed on catalyst preparations and characterization, and initiation of reaction studies. These activities are described in the following section comprising the experimental methodology and results.

#### **2.1 Methodology**

##### ***2.1.1 Catalyst Preparation [Clemson]***

Catalysts are being prepared according to the general formulation: 100-x)Fe/xMe/5Cu/17Si, where *Me* indicates a second-metal, and x is 10 or smaller. Second metals (*Me*) included in this stage of the project are Cr, Mo, W, Mn, Zr, Nb, Re, Sn, V, and Ta. As shown in the past two reports, our investigations started with chromium as the “second-metal” due to its known capacity to form mixed carbides with Fe. Fe-Cr mixed catalysts showed activities only slightly improved activities respect to a Fe-only catalyst, the standard catalyst, with the highest activity improvement at 5 mol % Cr. During this quarter, we have widened our search for mixed catalysts with significant higher Fischer-Tropsch synthesis activities using a wide variety of metals. As a starting point, a general formulation using 95Fe/5Me/17Si ratio has been assumed to prepare the new materials. The second metals and metal precursors for the new catalyst preparations are given in table 2. In general, catalysts have been prepared using the constant pH precipitation technique [1, 2]. Catalyst preparations make use of three solutions containing catalyst precursors at the desired molar ratio of components. Thus, for instance, the first solution contains  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (□0.6M) and a second metal precursor salt (concentration depends on the desired Fe/*Me* molar ratio) in water. A second solution contains tetraethylorthosilicate ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ , TEOS) dissolved in propanol. These two solutions are mixed first in a stirred round-bottom flask at  $83 \pm 3^\circ\text{C}$ . Once the temperature reaches  $83^\circ\text{C}$ , a third solution of aqueous  $\text{NH}_3$  (□2.7M) also at  $83 \pm 3^\circ\text{C}$  is added under vigorous and continuing stirring. The resulting pH after formation of a precipitated is 8.0-9.0. The precipitate is collected in an ice-cooled vessel and then thoroughly washed with deionized water (1.0 L water/10g of dry

weight material) to remove excess  $\text{NH}_3$ . The washed precipitate is dried in a vacuum oven for 48 h at 50 °C to remove excess water and then for an additional 12-24h at 120 °C. After drying, the catalyst precursor is calcined in air at 300 °C for 5 h in a muffle furnace. The calcined catalyst is sieved between 38-90  $\mu\text{m}$  before reaction testing and other characterizations.

**Table 2: List of second metals and metal precursors for mixed Fe/Me catalyst preparations**

Second Metal	Metal Precursor
Cr	$\text{CrO}_3$
	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
Mo	$\text{MoO}_3$
W	$\text{WO}_3$
	$\text{WO}_2$
	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$
	$\text{WCl}_6$
Zr	Zr(IV) dinitrate oxidehydrate
Mn	Mn(II) nitrate
Nb	Nb
Re	Re
Sn	Tin(IV) Acetate ( $\text{C}_8\text{H}_{12}\text{O}_8\text{Sn}$ )
V	Vanadium (III) acetylacetonate $\text{V}(\text{C}_5\text{H}_7\text{O}_2)_3$
Ta	Tantalum(V) Ethoxide $\text{Ta}(\text{OC}_2\text{H}_5)_5$

### 2.1.2 Catalyst Pretreatment

#### a) Passivation

To prevent the pretreated catalysts from rapidly oxidizing in air, H<sub>2</sub> reduced catalysts are passivated at room temperature using 2%O<sub>2</sub> in He for 1 hour.

#### b) Activation

Catalyst samples are pretreated in flowing either H<sub>2</sub> or CO at 280 °C for 12 h in a fixed bed reactor. The temperature program uses a 1 °C/min ramp from room temperature to 280 °C prior to the 12h pretreatment at this temperature.

### 2.1.3 Catalyst Characterization

Catalysts are characterized by elemental analysis, N<sub>2</sub> adsorption (BET, pore volume, pore size distribution), XRD (Fe and Me crystalline phases formed), and CO pulse chemisorption (surface metal atoms).

#### a) Elemental Analysis

Elemental analysis is performed to determine the composition of elements in the bulk of catalysts. The composition content of catalysts is determined using ICP-OES at Galbraith Laboratories.

#### b) N<sub>2</sub> Adsorption

The BET surface area, pore volume, average pore diameter, and pore size distribution of the catalysts are determined by N<sub>2</sub> physisorption using a Micromeritics ASAP 2010 automated system. A 0.3-0.5 g catalyst sample is degassed in the Micromeritics ASAP 2010 at 100 °C for 1 h and then at 300 °C for 2 h prior to analysis. The analysis is done using N<sub>2</sub> adsorption at -196 °C.

#### c) X-Ray Diffraction (XRD)

XRD is used to determine the phase composition of Fe catalysts as prepared and after pretreatments. The XRD spectrum of the catalysts is collected using an X-ray diffractometer, Scintag 2000 x-ray diffractometer, using monochromatized Cu K<sub>α</sub> radiation (40 kV, 40 mA) and a Ge detector using a step scan mode at a scan rate of 0.02° (2θ) per second from 10-80°. XRD peak identification is done by comparison to the JCPDS database software.

#### d) CO-Pulse Chemisorption

Fe dispersion is determined by pulsing carbon monoxide over the reduced catalyst. Approximately 0.2 g of catalyst is put in a quartz tube, incorporated in a temperature-controlled oven and connected to a thermal conductivity detector (TCD). The carrier gas used is helium. Prior to chemisorption, the catalyst is reduced in a flow of hydrogen (50 cc/min) at 280 °C for 12 h. Afterwards, the sample is purged with helium at 280 °C for 1 h and finally cooled down to room temperature. Carbon monoxide is pulsed at 35 °C over the reduced catalyst until the TCD signal is constant. An assumed stoichiometry ratio on the surface of CO:Fe<sub>s</sub><sup>0</sup> = 1:2 is used [3].

### 2.1.4 CO Hydrogenation Reaction Studies

CO hydrogenation is performed using 0.03 g of catalyst and 0.09 g of  $\alpha$ -alumina packed in a stainless steel microreactor. The total flow rate used is 50 ml/min with the H<sub>2</sub>/CO ratio of 10/1 or 2/1. The catalyst sample is pretreated at 280 °C for 12 h prior to CO hydrogenation. CO hydrogenation reactions are carried out at 280 °C and 1.8 atm total pressure. The product streams are analyzed by gas chromatography.

### 2.2 Results and Discussion

The first metal of the set of second metals on Table 2 to be studied has been Mo. Results for catalyst characterization are shown in Tables 3-5 and Figures 1-2. The CO hydrogenation activity of a mixed Fe/Mo catalyst is compared to that of the standard 100Fe catalyst and 90Fe/10Cr/5Cu/17Si catalyst in Figures 3-4.

Elemental analysis results are given in Table 3. The Mo content of a catalyst prepared according to the formula 90Fe/10Mo/5Cu/17Si was about 6 mol% providing the desired metal ratio.

**Table 3: Elemental analysis results for 90Fe/10Cr, 90Fe/10Mo catalysts and standard 100Fe catalyst.**

Sample	Element content (wt%)			mol%
	Fe	2 <sup>nd</sup> metal	Cu	2 <sup>nd</sup> metal
100Fe/5Cu/17Si (Standard)	51.60	0.00	1.91	0.00
90Fe/10Cr/5Cu/17Si	49.40	5.19	2.49	9.98
90Fe/10Mo/5Cu/17Si	50.20	5.52	3.37	6.00

BET surface areas, pore volumes, and average pore diameters of the Fe/Mo and Fe/Cr catalysts are given in Table 4. The standard 100Fe catalyst showed a BET surface area of 329 m<sup>2</sup>/g, a pore volume of 0.34 cm<sup>3</sup>/g, and an average pore diameter of 42 Å. The BET surface areas of 90Fe/10Cr and 90Fe/10Mo catalysts were similar, about 330 m<sup>2</sup>/g. Likewise, the pore volume and diameter values of 90Fe/10Cr and 90Fe/10Mo catalysts were 0.28 cm<sup>3</sup>/g and 40 Å, respectively. Thus, the second metal incorporation had no significant effect on surface and porosity characteristics of catalysts when compared to a 100Fe catalyst.

**Table 4: N<sub>2</sub> adsorption experimental results for Fe/Me mixed metal catalysts.**

Catalyst (after calcination at 300C 5hr)	N <sub>2</sub> Physisorption		
	BET s.a.(m <sup>2</sup> /g)*	Pore volume (cm <sup>3</sup> /g)	Average pore size (Å)
100Fe/5Cu/17Si (standard)	329	0.34	42
90Fe/10Cr/5Cu/17Si	331	0.28	34
90Fe/10Mo/5Cu/17Si	330	0.28	34

\* Using N<sub>2</sub> Physisorption at 77 K. Error of measurement = +/- 10%.

EXAFS experiments testing the K-edge for iron were undertaken during this quarter at the Center for Advanced Microstructures and Devices (CAMD) at LSU,. Tests run on were electron yield experiments that have surface-specific information of the iron in the catalysts (Figure 1). This information will be evaluated in conjunction with the November 2005 tests in transmission which can be used to determine bulk characteristics. Transmission experiments this quarter included the catalysts that newly synthesized catalysts from Clemson University that contain tungsten. The National Synchrotron Light Source (NSLS) at Brookhaven National Laboratories was used to test the molybdenum K-edge which is at 20 keV in electron yield experiments (Figure 2). The K-edge energy for Mo cannot be achieved at CAMD at a sufficient flux to achieve an optimum signal-to-noise ratio. Mathematical analysis and interpretation of these results will take place during the next quarter.

**Table 5: Catalysts used in analysis**

Catalyst tested in parts by mole (synthesized in Clemson University laboratories):
(1) 100 Fe – 5 Cu – 4.2 K – 11 SiO <sub>2</sub> calcined CO pretreat at 280 °C 12 h and passivate
(2) 90 Fe – 10 W – 5 Cu – 17 Si calcined CO pretreat at 280 °C 12 h and passivate
(3) 90 Fe – 10 W – 5 Cu – 17 Si calcined at 300 °C 5h
(4) 100 Fe – 5 Cu – 4.2 K – 11 SiO <sub>2</sub> calcined
(5) 90 Fe – 10 Mo – 5 Cu – 17 Si pretreat at 280 °C and passivate in O <sub>2</sub>
(6) 90 Fe – 10 Cr – 5 Cu – 17 Si calcined 300 °C 5h
(7) 100 Fe – 5 Cu – 17 Si pretreat in CO at 280 °C and passivate in O <sub>2</sub>
(8) 100 Fe – 5 Cu – 17 Si calcined 300 °C 5h
(9) 90 Fe – 10 W – 5 Cu – 17 Si prepared from WCl <sub>6</sub> calcined at 300 °C 5h
(10) 90 Fe – 10 W – 5 Cu – 17 Si calcined and CO pretreat
(11) 90 Fe – 10 Mo – 5 Cu – 17 Si calcined CO pretreat at 280 °C 12 h and O <sub>2</sub> passivate

Carbon monoxide hydrogenation reactions were carried out at 280 °C, 1.8 atm, and H<sub>2</sub>/CO ratio = 10 for all catalyst samples. The catalyst sample was reduced *in situ* in flowing H<sub>2</sub> at 280 °C for 12 h prior to CO hydrogenation. Figure 3 and 4 present CO hydrogenation total rates and % methane selectivity, respectively. At the reaction conditions used, both of 90Fe/10Cr and 90Fe/10Mo exhibited similar CO hydrogenation activity to the standard 100Fe catalyst. Initial methane selectivities of 90Fe/10Cr and 90Fe/10Mo were slightly less than that of the standard 100Fe catalyst. However, the steady state methane selectivity of all Fe/Cr catalysts, approximately 35-40%, was similar to that of the standard catalyst. In summary, the activity of catalyst with the addition of Cr and Mo as second metals was not higher than that of the standard 100Fe catalyst.

### 3.0 Conclusions

Reaction studies of Fe/Cr and Fe/Mo mixed metal catalysts showed that the CO hydrogenation activity for 90Fe/10Cr and 90Fe/10Mo catalysts was not higher than for the standard 100Fe catalyst.

### 4.0 Next Quarter's Activities

EXAFS experiments on the K-edge of copper will be carried out July in electron yield mode. Future tasks for the characterization of the mixed iron carbides will be to complete electron transmission and yield of the remaining elements: tungsten, molybdenum (only transmission left), chromium, and possibly silicon. Interpretation and analysis of the data obtained from the NSLS and CAMD during this quarter is underway. Determining how the bulk properties as well as the surface properties of the catalysts are affected by different compositions and different synthesis techniques will give the researchers an opportunity to hypothesize how the surface reactivity will change by changing these parameters. This data will also be able to be used in the future analysis of how and why the mixed carbides form at their respective locations. It is known that the location of the carbide and how it is coordinated with the metal will alter its reactivity, but how the different coordination effect the reactivity will be the objective of this part of the work.

CO hydrogenation activity studies are being conducted for catalyst using a wide range of other second metals. Results from these studies will be reported in the next quarter report.