

(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

Start Date: August 31, 2005

End Date: August 31, 2008

Presentations/Publications

None.

Patents

None.

Progress in Past Quarter and Current Status

A new graduate student has joined the catalyst research group at Clemson and is currently actively carrying out research tasks. Project activities are progressing in accordance to the project schedule (Table 1). During this first quarter of activities the main focus has been place on building the reaction system. In addition, initial preparations and basic characterization of catalysts have also been carried out. These activities are described in the following section comprising the experimental methodology and results. The NASEO grant was officially signed with Clemson in October. The subcontract to LSU was finalized in November and that to RTI is in final negotiation but should be signed by December 15.

5.2 Task Activities

5.2.1 Catalyst Preparation [Clemson]

Catalysts have been prepared according to the general formulation: $100-x)Fe/xMe/5Cu/4.2K/17SiO_2$, where *Me* indicates a second metal, and *x* is 10 or smaller. Second metals (*Me*) included in this initial stage of the project are Cr, Mo, and W, all group 6 elements known to form stable carbides. 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, a first solution contained $Fe(NO_3)_3 \cdot 9H_2O$ ($\square 0.6M$), and $Cu(NO_3)_2 \cdot 2.5H_2O$ in water. A second solution contained tetraethylorthosilicate ($Si(OC_2H_5)_4$) dissolved in propanol. These two solutions were mixed first in a stirred round-bottom flask at $83 \pm 3^\circ C$. Once temperature was $83^\circ C$, a third solution of aqueous

NH_3 ($\square 2.7M$) also at $83 \pm 3^\circ C$ was added under vigorous and continuing stirring. The resulting pH after formation of a precipitated was 8.0 - 9.0. The precipitate was 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 NH_3 . The washed precipitate was dried in a vacuum oven for 48 h at $50^\circ C$ to remove excess water and then for an additional 12-24h at $120^\circ C$. After drying, the catalyst precursor was calcined in air at $300^\circ C$ for 5 h in a muffle furnace. The calcined catalyst was

sieved between 38-90 μm before reaction testing and other characterizations. For mixed metal catalysts, precursors for the second metal (Cr, Mo, W) were mixed within the initial precursors' solution at the desired molar ratio.

5.2.2 Catalyst Characterization [Clemson, LSU]

Catalysts have been characterized by elemental analysis, N_2 adsorption (BET, pore volume, pore size distribution), CO chemisorption (surface metal atoms), XRD (Fe and Me crystalline phases formed) and TPR (reducibility of the metal phases).

a) Elemental Analysis

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

b) N_2 Adsorption

The BET surface area, pore volume, average pore diameter, and pore size distribution of the catalysts were determined by N_2 physisorption using a Micromeritics ASAP 2010 automated system. A 0.3-0.5 g catalyst sample was degassed in the Micromeritics ASAP 2010 at 100 $^\circ\text{C}$ for 1 h and then at 300 $^\circ\text{C}$ for 2 h prior to analysis. The analysis was done using N_2 adsorption at -196 $^\circ\text{C}$.

c) X-Ray Diffraction (XRD)

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

d) CO-Pulse Chemisorption

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

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e) Chemisorption

H_2 and CO chemisorption were carried out to determine the surface Fe atoms using a Micromeritics ASAP 2010. Prior to chemisorption, 0.5 g of catalyst was reduced in a flow of H_2 (50 cc/min) at 280 $^\circ\text{C}$ for 12 h. Afterwards, the sample was purged with helium at 280 $^\circ\text{C}$ for 1 h and finally cooled down to room temperature. H_2 chemisorption was performed at 35 $^\circ\text{C}$. The assumed surface stoichiometry for $\text{H}:\text{Fe}_s^0$ was 1:1.

5.2.3 Reaction System

Figure 1: Schematic representation of the Clemson reaction system built for reaction studies.

REACTOR

H

2

To

GC

To MS

Differential
Pump

6-port valve

Bleed Valve

MFC3

Filter

MFC3

Filter

MFC3

Filter

He

CO/5%Ar

H₂O Saturator

Filter

MFC2

13

CO

1

2

4

3

Filter

MFC2

12

CO

Vent

1

2

3

4

5

6

Pressure
Transducer

Back Pressure
Regulator

Switching Valve

H₂O in

Vent

He

Bypass

Pressure
Transducer

Back Pressure
Regulator

5

The system constructed consists of a differential flow reactor connected to a gas chromatograph and mass spectrometer, as shown in Figure 1. The catalyst is placed in a 0.3 in. (7.6 mm) I.D. stainless steel reactor. The pressure in the reactor is kept constant at 1.8 atm using a back pressure regulator. A thermocouple is placed at the bottom of the catalyst bed. For SSITKA studies, a Valco two-position valve with an electric actuator is used to switch between the ¹²CO and labeled ¹³CO. The reactor outlet is connected to a gas chromatograph (Varian CP-3380) and a quadrupole mass spectrometer (Pfeiffer Vacuum). A part of the reaction effluent is introduced into the mass spectrometer via a 1/16 inch capillary tube and differential pumping. A 6-port sampling valve is placed between the reactor outlet and the GC. In the GC, a 6-ft long 80/100 mesh carbosphere column (Alltech) equipped with a thermal conductivity detector is used to analyze CO, H₂, and CO₂ in the feed and product streams. The composition of hydrocarbons in the product stream is analyzed by a Porapak Q column equipped with a flame ionization detector. The GC conditions for the two modes of operation are shown in the Table 2.

Table 2: Conditions for the GC operation.

Gas Chromatograph	Varian CP-3380	Varian CP-3380
Detector	TCD	FID
Column	carbosphere	Porapak Q
Carrier gas	He (99.999%)	He (99.999%)
Carrier gas flow	30 ml./min.	30 ml./min.
Column temperature	120 °C	120 °C
- Initial	120 °C	120 °C
- Final	220 °C	130 °C
Detector temperature	35 °C	35 °C
Injector temperature	CO, H ₂ , and CO ₂	Hydrocarbon C ₁ -C ₇
Analyzed gas		

5.3 Results

Results for catalyst characterization are shown in Tables 3-5.

Table 3: Elemental analysis results for mixed metal catalysts prepared using metals from the group 6 (Cr, Mo, W).

Sample	Element content (wt%)			mol%	Na residue (ppm)
	Fe	M	Cu		
100Fe/5Cu/17Si (pH9)	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	5.75	-
90Fe/10W/5Cu/17Si	41.80	12.20	2.00	6.64	506.00

M represents the percentages amounts for second metal (Cr, Mo, or W).

Table 4: N₂ adsorption experimental results for iron catalysts and mixed metal catalysts.

Catalyst (after calcination at 300C 5hr)	N ₂ Physisorption		
	BET s.a.(m ² /g)	Pore volume ³ (cm ³ /g)	Average pore size (Å)
100Fe/5Cu/4.2K/11PSiO2#1	142.00	0.14	40.00
100Fe/5Cu/17Si(pH 9)	329.00	0.34	42.00
90Fe/10Cr/5Cu/17Si	331.00	0.28	34.00
90Fe/10Mo/5Cu/17Si	330.00	0.28	34.00
90Fe/10W/5Cu/17Si	296.00	0.22	30.00

#1: Data obtained for a catalyst using a different amount of silica precursor.

Table 5: CO chemisorption data for the iron catalyst and iron-chromium mixed metal catalysts.

	100Fe/5Cu/17Si	90Fe/10Cr/5Cu/17Si
%Fe Loading	51.60%	49.40%
Sample Wt.(g)	0.11	0.10
Metal(g)	0.06	0.05
Molecule/g	6.21E+20	5.49E+20
Vol. Adsorbed CO (μl)	55.61	53.80
Vol. (μL) of CO 1mol	2.49E+07	2.49E+07
CO Molecules Adsorbed	1.35E+18	1.30E+18
Active Site/g	2.42E+19	2.53E+19
%Metal Dispersion	3.89	4.60

Elemental analysis shows the incorporation of the second metal on the bulk oxide of the iron catalysts. The residual sodium amount on the sample containing W is a consequence of using sodium metatungstate as the W precursor. As expected, increasing the silica content increased the resulting BET area and total pore volume (Table 4). CO chemisorption showed characteristic metal dispersion of about 4%. Reaction studies with these catalysts will start during the next quarter.

Several of the catalysts prepared to date have been sent to LSU and will be examined in December by XAFS for baseline purposes.

4 Conclusions

The project has started and is on track. A graduate student has joined the catalyst research group at Clemson. A reaction system to test catalyst samples from different mixed metal preparation has now been built at Clemson and is ready for use. The initial set of metals to be used in the preparation of mixed metal catalysts is Cr, Mo, and W, all metals from the group 6 of the periodic table. These family of metals form stable carbides and are known to form mixed carbides with Fe. Several initial preparations have been made, including a baseline catalyst. The catalysts have been partially characterized to date. XAFS will be done at LSU in December to establish that methodology.

References

1. Bukur, D.B., Lang, X., Rossin, J.A., Zimmerman, W.H., Rosynek, M.P., Yeh, E.B., and Li, C., *Ind. Eng. Chem. Res.* 28, 1130 (1989).
2. Jothimurugesan, K., Goodwin, J.G. Jr., Gangwal, S.K., and Spivey, J.J., *Catal. Today* 58, 335 (2000).
3. Sudsakorn, K., Goodwin, J.G. Jr., and Adeyiga, A.A., *J. Catal.* 213, 204 (2003).

6. Plans for Next Quarter:

During the next quarter, more catalysts will be prepared varying the second metal content and efforts will be carried out to determine pretreatment conditions allowing the formation of mixed metal carbides. XAFS studies will begin at LSU on the catalysts being studied in order to refine our techniques for identifying the phases of carbide produced in the catalysts initially and with reaction time-on-stream. Reaction studies will begin at Clemson of the base catalyst (for comparison) and FeCr mixed metal catalysts. 8