

(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

Tasks	Activity											
	Year 1				Year 2				Year 3			
	1	2	3	4	1	2	3	4	1	2	3	4
Task 1: Catalyst Prep.		X		X		X		X		X		X
Task 2: Catalyst Charac.	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
Task 4: Slurry Phase Reactor Testing		X		X		X		X		X		X
Task 5: Eval. of Comm. Potential				X			X			X		
Reports				X			X			X		

Table 1: Project Schedule

Project activities are progressing in accordance with the project schedule (Table 1). During this second quarter of activities the main focus has been place 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 initial stage of the project are Cr, Mo, and W, all group VI elements known to form stable carbides. Chromium is the “second-metal” we have started our investigations with due to its known capacity to form mixed carbides with Fe. 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 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\square 0.6\text{M}$), CrO_3 (concentration depends on the desired Fe/Cr molar ratio) and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in water. A second solution contains tetraethylorthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$) 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 reached 83°C , a third solution of aqueous NH_3 ($\square 2.7\text{M}$) 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 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 μm before reaction testing and other characterizations.

2.1.2 Catalyst Pretreatment

a) Passivation

To prevent the pretreated catalysts from rapidly oxidizing in air, the catalysts are passivated at room temperature using 2% O_2 in He for 1 hour.

b) Activation

Because Fe oxides are not active for CO hydrogenation, catalysts have to be activated prior to CO hydrogenation. The catalyst sample is pretreated in flowing either H_2 or CO at 280°C for 12 h in a fixed bed reactor. The temperature program uses a $1^\circ\text{C}/\text{min}$ ramp from room temperature to 280°C prior to the 12h pretreatment at this temperature.

2.1.3 Catalyst Characterization

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 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) N₂ Adsorption

The BET surface area, pore volume, average pore diameter, and pore size distribution of the catalysts are determined by N₂ 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 N₂ 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_α 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_s⁰ = 1:2 is used [3].

e) H₂ Chemisorption

H₂ chemisorption is carried out to determine the surface Fe atoms using a Micromeritics ASAP 2010. Prior to chemisorption, 0.5 g of catalyst is reduced in a flow of H₂ (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. H₂ chemisorption is performed at 35 °C. The assumed surface stoichiometry for H:Fe_s⁰ is 1:1.

f) Extended X-ray absorption fine structure (EXAFS)

EXAFS is used to provide information on the structure and coordination of atoms on the catalyst surface. The catalysts studied to date and their preparation conditions are listed in Table 2. The data collection parameters are provided in Table 3. The concentrations of the elements are such that measurement in transmission was possible. Germanium 220 (Ge 220) crystals are used for all elements. The heavier elements are analyzed in air.

Table 2: Catalysts, their compositions, pretreatments, and absorption edges investigated

Catalyst	Calcined at 300°C for 5 hours	CO pre-treated at 280°C for 12 hours and passivated in 2% O ₂
Absorption Edges		Absorption Edges
100Fe/5Cu/17Si	Fe, Cu	Fe, Cu
90Fe/10Cr/5Cu/17Si	Fe, Cu, Cr	Fe, Cu, Cr

Table 3: Data collections parameters

Edge	Energy Range (eV)	Step Size (eV)		Integration Time (sec)
Chromium	K	5850,5980,6040,6990	3,0.3,2	1.0
Iron	K	6955,7100,7170,8100	3.0,0.3,2.0	1,1,1
Copper	K	8830,8960,9040,9880	3.0,0.4,2.0	1.0

2.1.4 CO Hydrogenation Reaction Studies

CO hydrogenation is performed using 0.03 g of catalyst and 0.09 g of α -alumina packed in a stainless steel microreactor. The total flow rate used is 50 ml/min with the H₂/CO ratio of 10/1. 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

During this quarter, research was focused on the effect of Cr loading of Fe/Cr mixed metal catalysts in the CO hydrogenation activity. Thus, catalysts with Fe/Cr ratios: 99Fe/1Cr, 97Fe/3Cr, 95Fe/5Cr, 93Fe/7Cr, and 90Fe/10Cr were prepared using the precipitation technique. Results for catalyst characterization are shown in Tables 4-6 and Figures 1-2. The CO hydrogenation results are presented in Figures 3-4.

Elemental analysis results are given in Table 4. The Cr content of a catalyst prepared according to the formula 90Fe/10Cr/5Cu/17Si was about 9.98 mol%, meaning that the precipitation technique used was able to yield catalysts with the desired metal ratios.

Table 4: Elemental analysis results for 90Fe/10Cr catalyst and reference 100Fe catalyst.

Sample	Element content (wt%)			mol%
	Fe	Cr	Cu	Cr
Fe/M/Cu/Si				
100Fe/5Cu/17Si (Standard)	51.60	0.00	1.91	0.00
90Fe/10Cr/5Cu/17Si	49.40	5.19	2.49	9.98

BET surface areas, pore volumes, and average pore diameters of the Fe/Cr catalysts are given in Table 5. The standard 100Fe catalyst showed a BET surface area of 329 m²/g, a pore volume of 0.34 cm³/g, and an average pore diameter of 42 Å. The BET surface areas of the Fe/Cr catalysts with different Cr loadings were in the range 331-358 m²/g. Likewise, the pore volume and diameter values of Fe/Cr catalysts were 0.28-0.32 cm³/g and 29-38 Å, respectively. Thus, Cr incorporation had no significant effect on surface and porosity characteristics of catalysts when compared to a 100Fe catalyst.

Table 5: N₂ adsorption experimental results for Fe/Cr mixed metal catalysts.

Catalyst (after calcination at 300C 5hr)	N ₂ Physisorption		
	BET s.a.(m ² /g)*	Pore volume (cm ³ /g)	Average pore size (Å)
100Fe/5Cu/17Si (standard)	329	0.34	42
99Fe/1Cr/5Cu/17Si	339	0.32	38
97Fe/3Cr/5Cu/17Si	346	0.29	34
95Fe/5Cr/5Cu/17Si	351	0.29	33
93Fe/7Cr/5Cu/17Si	358	0.26	29
90Fe/10Cr/5Cu/17Si	331	0.28	34

* Using N₂ Physisorption at 77 K. Error of measurement = +/- 10%.

Chromium incorporation at these levels in the Fe catalyst does not significantly affect its CO chemisorption capacity, see Table 6.

Table 6: CO chemisorption data for 90Fe/10Cr catalyst and reference 100Fe catalyst.

Catalyst	CO chemisorption	
	Total (μmol CO/gcat)	% Fe Dispersion
100Fe/5Cu/17Si	20.06	3.89
90Fe/10Cr/5Cu/17Si	20.99	4.6

The iron K edge spectra of the 90Fe/10Cr catalyst and reference 100Fe catalyst from EXAFS are plotted in Figure 1. The spectrum of iron metal is also shown for comparison. Before pre-treatment, all Fe species in the different catalysts had the same oxidation state. Pre-treatment reduces the oxidation state of Fe to a very similar level in reference 100Fe catalyst, however the average oxidation state of the chromium-bearing one is little higher. Pre-treatment of all these catalysts should yield some form of Fe carbide, along with other iron phases. Suitable Fe carbide standards have yet to be measured.

Carbon monoxide hydrogenation reactions were carried out at 280^o C, 1.8 atm, and H₂/CO ratio = 10 for all catalyst samples. The catalyst sample was reduced *in situ* in flowing H₂ at 280^o 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, 95Fe/5Cr exhibited approximately a 30% higher CO hydrogenation activity than the

standard 100Fe catalyst. The activities of other Fe/Cr mixed catalysts were similar to that observed for the standard 100Fe catalyst. On the other hand, initial methane selectivities of 97Fe/3Cr, 95Fe/5Cr, and 93Fe/7Cr were significantly less than that of the standard 100Fe catalyst. However, the steady state methane selectivity of all Fe/Cr catalysts, approximately 35-37%, was similar to that of the standard catalyst.

3.0 Conclusions

The project is meeting its goals. The results in this quarter show that for Fe/Cr mixed catalysts there is an optimum Fe/Cr ratio for highest catalytic activity around 5 mol % Cr. Chromium, however, seems to hamper Fe reducibility, as show by EXAFS, which may be affecting the ability of surface Fe to form carbides at a compositions >5%, hindering catalyst activity.

Plans for Next Quarter:

The study of FeCr is planed to be largely completed in the next quarter. Preparation of a series of FeMo catalysts and their study will begin.

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., Gangwal, S.K., and Spivey, J.J., *Catal. Today* **58**, 335 (2000).
3. Sudsakorn, K., Goodwin, J.G., and Adeyiga, A.A., *J. Catal.* **213**, 204 (2003).