

(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	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	X	X	X	X	X
Task 5: Eval. of Comm. Potential				X	X	X	X	X	X	X	X	X
Reports				X	X	X	X	X	X	X	X	X

Table 1: Project Schedule

Project activities are progressing in accordance with the project schedule (Table 1). 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

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. During this quarter, we have prepared Fe based catalysts with 5 mol% of Cr, Mo, W, Mn, Zr, V and Ta 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; $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (~0.6 M), $\text{Cu}_2\text{O} \cdot 3\text{H}_2\text{O}$ and tetraethylorthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS).

The first 2 solutions are

dissolved in 60 ml of water where the latter is dissolved in 40 ml of propanol in order to obtain total volume of 100 ml. Second metal precursors used are given below in Table 1 for which its concentration depends on the desired Fe/Me molar ratio. Then the solutions are mixed first in a stirred round-bottom flask at $83 \pm 3^\circ\text{C}$. Once the temperature reaches 83°C , aqueous NH_3 (~2.7 M) also at $83 \pm 3^\circ\text{C}$ is slowly added under vigorous and continuing stirring for 3 min. The resulting pH after formation of a precipitated is 8-9. The precipitate is aged in a vessel at room temperature for 17-18 h then thoroughly washed with deionized water to remove excess NH_3 until pH is 7-8 (1.3-1.5 liters of deionized water used). The washed precipitate is dried in an oven for 18-24 h at 120°C to remove excess water. After drying, the catalyst precursor is calcined in static air at 300°C for 5 h, then cooled to room temperature over a 2-h period in a muffle furnace. A fresh calcined catalyst is sieved $< 90 \mu\text{m}$ before reaction testing and other characterizations.

2.1.2 Catalyst Characterization

Catalysts are characterized by elemental analysis, N_2 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_2 Adsorption

The BET surface area, pore volume, average pore diameter, and pore size distribution of the catalysts are determined by N_2 physisorption using a Micromeritics ASAP 2010 automated system. A 0.3 g catalyst sample is degassed in the Micromeritics ASAP 2010 at 100°C for 1 h and then at 300°C for 2 h with $10^\circ\text{C}/\text{min}$ ramping rate prior to analysis. The analysis is done using N_2 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 CO 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). He is used as a carrier gas for this system. 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 cooled down to 35°C with He 30cc/min. CO is pulsed at 35°C over the reduced catalyst until the TCD signal is constant. An assumed stoichiometry ratio on the surface of $\text{CO}:\text{Fe}_s = 1:2$ is used [3].

e) 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 are studied at the Center for Advanced Microstructures and Devices (CAMD).

2.1.3 CO Hydrogenation Reaction Studies

CO hydrogenation is performed using 0.1 g of catalyst packed in a fixed bed-quartz reactor with i.d. = 8 mm. The total flow rate used is 60 cc/min with the H₂/CO ratio of 2/1 in a balance of He. The catalyst sample is pretreated in 30 cc/min of H₂ at 280 °C for 12 h with 2 °C/min ramping rate prior to CO hydrogenation.

CO hydrogenation reactions are carried out at 280 °C and at 1.8 atm. The product streams are analyzed by gas chromatography.

2.2 Results and Discussion

During this quarter, catalysts were characterized by EXAFS determining the K-edge for copper spectra. The list of catalysts and electron yield obtained for the K-edge for copper are shown in Table 2 and Figure 1, respectively. The electron yield experiments are surface-specific for copper. Due to the low loading of Cu (especially since the majority of Cu is expected to be in the bulk), the detection limits for electron yield are being approached. For accurate EXAFS data, the signal-to-noise ratio must be approximately 100:1, therefore only the XANES data were taken (the XANES region is within ~30 eV of the edge) [4]. The XANES data will be used to determine oxidation state and average coordination number of the copper atoms. This can be useful to determine differences in the reducibility of the catalysts (copper is a reduction promoter for Fe).

X-ray diffraction data were also taken to supplement XAS (x-ray absorption spectroscopy) data. These experiments were designed to determine what crystalline phases are present in the catalysts. The four tungsten containing catalysts were tested using XRD on the Rigaku Miniflex which uses excitation. Due to the high iron loading, it was expected to yield undesirable results, which was proven to be true as shown in Figure 3. An upgrade to the XRD at CAMD is now complete. In addition to having a 10 α KCu⁴ increase in resolution, the synchrotron line has the advantage of being tunable to Fe excitation, which will allow for orders of magnitude improved resolution. The data on the Rigaku Miniflex was taken on standard tape, while the data at CAMD will be taken on a noise-free sample holder (Si based) [5].

Table 3: Variations in catalyst activity and selectivity for various Fe-based mixed catalysts at the maximum reaction rate.

Catalyst ^a	Max rate ^b ($\mu\text{mol/g/s}$)		% Selectivity		% Olefin (C ₂ -C ₄)					
	CO ₂	total HC	CO ₂	C ₁	C ₂	C ₃	C ₄	C ₅ ⁺		
100Fe	0.36	0.38	34	29	21	27	14	9	58	
95Fe/5Cr	1.15	0.83	43	32	17	24	16	10	53	
95Fe/5Mo	0.64	0.46	43	29	18	25	18	10	58	
95Fe/5Mn	0.88	0.63	43	29	24	24	15	8	58	
95Fe/5Ta	0.56	0.53	36	32	17	26	16	9	57	
95Fe/5V	0.68	0.58	39	32	18	25	15	10	56	
95Fe/5W	0.19	0.29	26	32	21	28	14	4	62	
95Fe/5Zr	1.78	1.16	46	32	18	23	15	11	53	

Table 4: Variations in catalyst activity and selectivity for various Fe-based mixed catalysts at 300 min TOS.

Catalyst ^a	SS rate ^b (μmol/g/s)		% Selectivity	% Olefin (C ₂ -C ₄)				α (C ₃ - C ₆) C ₅ ⁺		
	CO ₂	total HC	CO ₂	C ₁	C ₂	C ₃	C ₄			
100Fe	0.11	0.20	23	26	29	26	13	6	74	0.28
95Fe/5Cr	0.25	0.28	33	29	26	25	13	8	75	0.38
95Fe/5Mo	0.19	0.21	31	28	27	25	14	6	72	0.28
95Fe/5Mn	0.24	0.30	31	31	27	25	12	5	73	0.36
95Fe/5Ta	0.12	0.21	23	27	27	25	14	6	74	0.38
95Fe/5V	0.21	0.26	31	29	27	25	13	7	72	0.36
95Fe/5W	0.11	0.18	25	29	28	26	13	4	68	0.36
95Fe/5Zr	0.32	0.33	35	31	27	23	12	6	74	0.40

The water gas shift activity appeared to be promoted by the addition of Cr, Mo, Mn, V or Zr showing higher %selectivity to CO₂ compared to unpromoted Fe catalyst (approximately 30% enhancement). These second metals also had a positive impact on α (a probability of chain growth propagation) by increasing it ca. 35%. On the other hand, none of these second metals affected significantly the selectivity towards methane or the %C₂-C₄ olefins. Adding W did not improve catalyst activity, exhibiting lower CO hydrogenation and water gas shift activities. A possibility of a Cl impurity in the catalyst may have caused this but we are not completely certain of this. Elemental analysis on this catalyst will be done in the future.

TOS behavior of CO₂ formation rate at 280 °C with the addition of Cr, Mn, V, Zr, Mo, Ta or W is shown in Figures 3 and 4. Also, Figures 5 and 6 show activity and deactivation of catalysts for total hydrocarbon products at 280 °C.

Zr, Cr and Mn appeared to offer the greatest potential for improving the FTS properties of the Fe catalyst. The catalyst activity was most enhanced by the addition of Zr. The water gas shift and Fischer-Tropsch reaction activity of 95Fe/5Zr was 3 times higher than that of 100Fe. All of the catalysts studied here showed the existence of a reaction induction period which has been hypothesized to be due to the formation of active mixed Fe carbides on the catalyst surface. It took about 15 – 20 min after syngas was introduced to the reactor for the catalysts to exhibit their maximum activities. However, the FeZr catalyst did not exhibit this induction phenomenon for the production of hydrocarbons, unless it was shorter than 5 min TOS. Thus, future research will address the question of why Zr doped catalysts showed this different behavior.

3.0 Conclusions

Reaction studies showed that the addition of Cr, Mo, Mn, Ta, V or Zr as a second metal for the Fe mixed catalyst is able to significantly enhance the CO hydrogenation and water gas shift activity compared to the benchmark Fe catalyst. FeZr shows the most improvement in the catalyst activity followed by FeCr and FeMn. These formulations offer exciting possibilities for the development of improved Fe FTS catalysts.

4.0 Next Quarter's Activities

An FeZr catalyst (95Fe/5Zr/5Cu/17Si) shows an extremely interesting higher activity for CO hydrogenation and for the water gas shift reaction than do 95Fe/5Cr/5Cu/17Si and 95Fe/5Mn/5Cu/17Si. Research in the next quarter will focus on these 3 catalysts by varying % second metal loading. In the

same time, an EXAFS study is underway to complete *ex situ* electron transmission and yield of the remaining elements: tungsten, molybdenum (only transmission left), chromium, and possibly silicon, as well as to investigate the interactions of Zr with Fe in the reduced catalyst during reaction. The catalysts will be run in XRD at CAMD when the beamline is online. Data interpretation of data acquired is in the process of being interpreted, and will be available in the upcoming months. BET surface area, CO pulse chemisorption and XRD will be performed for all the catalysts shown in this report during the next quarter.

References

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