

(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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Public Abstract

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

Research is being carried out that addresses the need for highly active, selective, attrition resistant and stable iron-based catalysts for converting low H₂/CO ratio syngas from coal and biomass to clean fuels, additives, and lubricants using the Fischer-Tropsch synthesis (FTS). The 36-month research project involves **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), 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 CO₂, its use as a fuel feedstock is attractive because this results in virtually no net CO₂ 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 H₂/CO ratio syngas to fuels via FTS. These relatively low-cost catalysts have low methane selectivity and high water gas shift activity (which generates H₂ *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 addresses 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 focuses on the ability of second and third metals to form mixed-metal carbides with Fe at reaction or pretreatment conditions. Improvements in activity should result as catalytically active surface carbide structures are stabilized in the

presence of H₂O and CO₂, important for use at the high conversions required for commercial operation. This should also result in a decrease in the rate of deactivation, thereby improving the longevity of the catalyst. Interesting selectivities, especially low methane production, should result as we modify the nature of the active surface carbide and, potentially, the active sites. The catalysts synthesized will be studied using Fischer-Tropsch synthesis (high pressure gas phase, steady-state isotopic transient kinetic analysis, slurry phase including with a slurry bubble column reactor) and detailed characterization (x-ray absorption fine structure, x-ray diffraction, chemisorption, attrition testing, among others). The results from the various studies compared to the benchmark catalyst will then be used to evaluate commercial potential.

1.0 Statement of Project Objectives

The objective of the research project is 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 addresses 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 focuses 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 should result as we better stabilize catalytically active surface carbide structures in the presence of H₂O and CO₂, important for use at the high conversions required for commercial operation. This should also result in a decrease in the rate of deactivation, thereby improving the longevity of the catalyst. Interesting selectivities, especially low methane production, may result as we modify the nature of the active surface carbide and, potentially, the active sites. The catalysts will be prepared, using methodology developed by members of the team at RTI and Clemson, to be attrition resistant so that they can be used in slurry phase reaction in an SBCR.

2.0 Project Activities

Project activities are progressing in accordance with the project schedule (Table 1) except for Tasks 4 & 5 which are delayed by contract issues. During this quarter the main focus has been on preparing Fe catalysts with K and Mn addition by varying %loading and on studying their catalytic activities. These activities are described in the following section comprising the experimental methodology and results.

Table 1: Project Schedule

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	
Task 2: Catalyst Charac.	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
Task 4: Slurry Phase Reactor Testing			X	X			X	X		X	X	
Task 5: Eval. of Comm. Potential					X				X			X

2.1 Methodology

2.1.1 *Catalyst Preparation*

Catalysts were prepared according to the general formulation, 100Fe/5Cu/17Si and (100-x)Fe/xMe/5Cu/17Si (on an atomic basis) where *Me* is Cr, Mn or Zr and x is 20 or smaller, using the constant pH precipitation technique [1]. First, Fe(NO₃)₃·9H₂O (~0.6 M) and CuN₂O₆·3H₂O were added together into 40 ml of H₂O while Cr(NO₃)₃, Mn(NO₃)₂ or ZrO(NO₃)₂ was added into 20 ml of H₂O. Tetraethylorthosilicate (Si(OC₂H₅)₄, TEOS) was added into 40 ml of propanol. Then the solutions were mixed together and heated to 83 ± 3°C. In the same time, NH₄OH (~2.7 M) was heated to 83 ± 3°C. After reaching 83°C, aqueous NH₄OH was slowly added into the mixed solution containing Fe, Cu, Si and Mn precursors under vigorous stirring until the solution was precipitated and pH was 8-9. The precipitate was aged in a vessel at room temperature for 17 h and thoroughly washed with deionized water to remove excess NH₃ to obtain the pH of 7-8 (1.3-1.5 liters of deionized water used). The washed precipitate was dried in an oven for 18-24 h at 110°C and was sieved < 90 μm. The catalyst precursor was calcined in static air at 300°C for 5 h, and then cooled to room temperature over a 2-h period in a muffle furnace.

2.1.2 *Catalyst Characterization*

Catalysts were characterized by elemental analysis, N₂ adsorption (BET, pore volume, pore size distribution), XRD (Fe and *Me* crystalline phases formed), and CO pulse chemisorption (surface metal atoms), and EXAFS (the structure and coordination of Fe atom).

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 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°C/min ramping rate 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 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 CO:Fe_s⁰ = 1:2 is used [2].

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) at LSU.

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.

2.1.4 Steady-State Isotopic Transient Kinetic Analysis (SSITKA)

SSITKA was performed by switching ¹²CO (containing 5% Ar) and ¹³CO without disturbing the other reaction conditions using a Valco 2-position valve with an electric actuator. The total flow rate and reaction pressure of these 2 feed streams were identical during the switch. A small trace of Ar was present in the unlabelled ¹²CO stream in order to measure the gas-phase

holdup for the reaction system. The reaction was carried out at the same conditions as given above except that a H₂:CO ratio of 20:1 was used in order to obtain CH₄ as the primary product. The effluent gas was analyzed online by mass spectrometer (MS) and Balzers Quadstar 422 v 6.0 software. Surface kinetic parameters such as the average surface residence time of CH₄ and CO (τ_{CH_4} and τ_{CO}) were determined from the isotopic transients using SSITKA data analysis software.

2.2 Results and Discussion

During this quarter, we have investigated the impact of Cr and Zr addition at various %loadings on the Fe-based catalyst for CO hydrogenation. The formulation of catalysts studied were (100-x)Fe/xMe/5Cu/17Si where x varied from 3-14 atomic% and Me = Cr or Zr. The activities of prepared FeCr and FeZr catalysts were compared to FeMn, as reported in the 7th quarterly report, and the benchmark catalyst, 100Fe/5Cu/17Si.

Activities of Fe-based catalysts with varying concentrations of added Cr, Mn, or Zr were investigated at 280°C, 1.8 atm with a H₂/CO ratio of 2:1 and are shown in Figs. 1, 2 and 3, respectively, for (a) CO hydrogenation and (b) the WGS reaction. The activities of all the Fe catalysts went through similar induction periods for both reactions, regardless of the type or the concentration of added metal. This induction period took approx. 15 min TOS at these reaction conditions. The existence of the reaction induction period has been reported to be due to the time required for the conversion of α -Fe to Fe carbides [3].

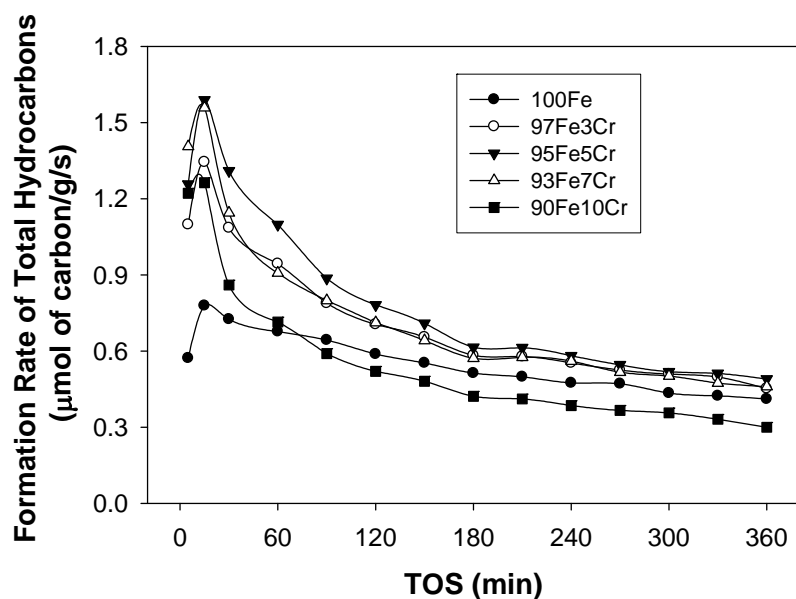


Figure 1 (a): Formation rate of hydrocarbon products at 280°C with the addition of various Cr concentrations.

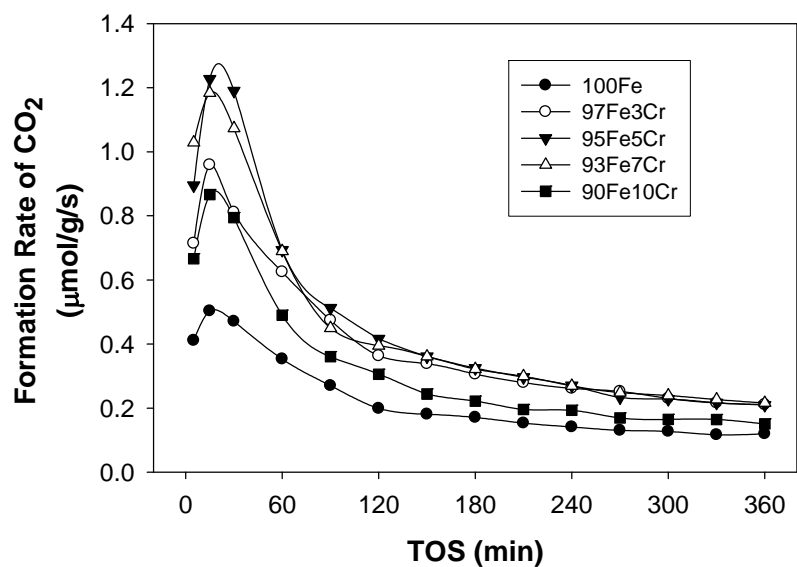


Figure 1 (b): Formation rate of CO₂ at 280°C with the addition of various Cr concentrations.

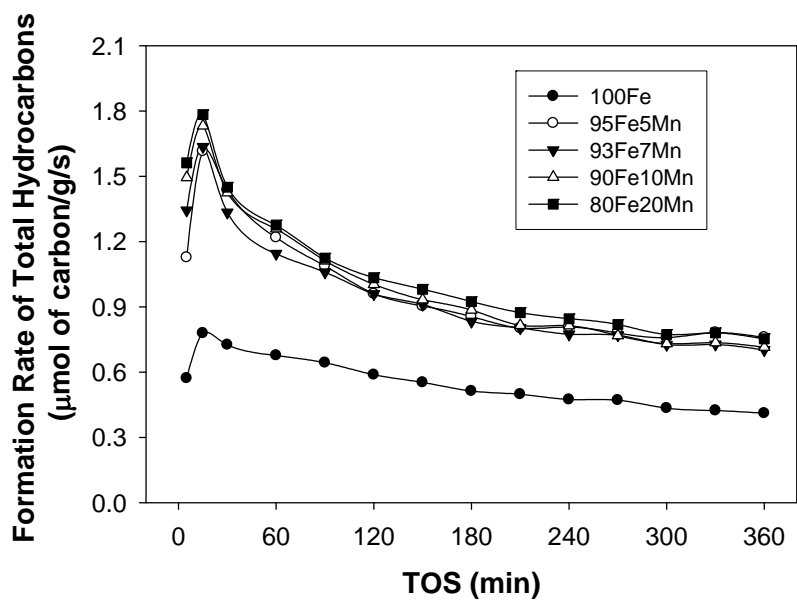


Figure 2 (a): Formation rate of hydrocarbon products at 280°C with the addition of various Mn concentrations.

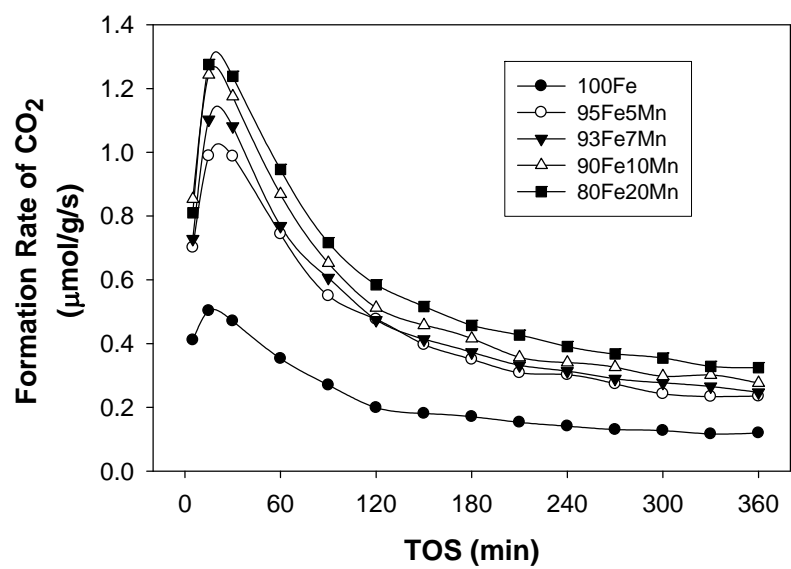


Figure 2 (b): Formation rate of CO₂ at 280°C with the addition of various Mn concentrations.

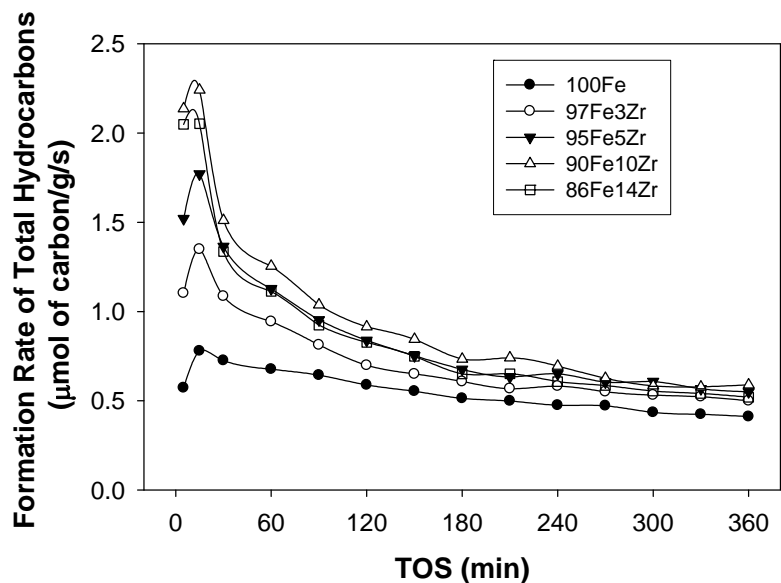


Figure 3 (a): Formation rate of hydrocarbon products at 280°C with the addition of various Zr concentrations.

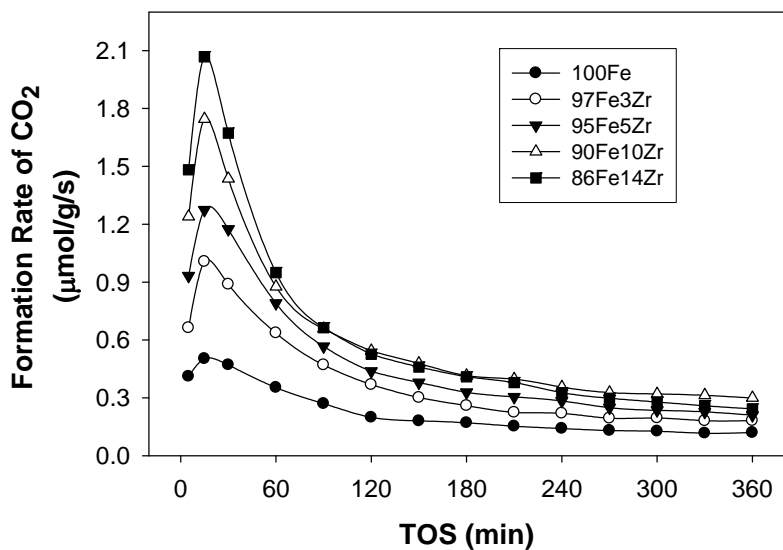


Figure 3 (b): Formation rate of CO₂ at 280°C with the addition of various Zr concentrations.

Figs. 1 (a) and (b) clearly shows that adding Cr at low concentrations (3-7 atomic%) had a positive impact on the activities of the catalysts while further addition of Cr only increased the deactivation rate of catalyst. On the contrary, the formation rates of hydrocarbon products and CO₂ appeared to increase with increasing %Mn (to 20 atomic%) and Zr (to 14 atomic%) loading (Figs. 4 and 5, respectively). The activities of the FeMn catalysts were at least twice as much as those observed for the benchmark 100Fe catalyst. The initial activities of the Fe catalyst for both

CO hydrogenation and the WGS reaction were significantly impacted by the concentration of added Zr [Figs. 3 (a) and (b)]. The formation rate of hydrocarbons and CO₂ during the induction period increased considerably with increasing Zr content. 90Fe10Zr and 86Fe14Zr exhibited significantly high activity, showing almost no induction period. Berry et al. [4] has proposed that Zr⁺⁴ can interact with O atoms of CO, thus weakening the C-O bond and, consequently, increasing carbide formation. Although O'Brien et al. [5] reported that the addition of Zr to an ultrafine Fe catalyst did not improve the catalyst activity, this divergence in results may have been due to difference in catalyst compositions and preparation.

Table 2: Catalyst activities and selectivities for Fe-based catalysts with the addition of Cr, Mn, or Zr.

Catalyst ^a	Maximum rate ^b (□mol of C/g/s)		SS rate ^{b,c} (□mol of C/g/s)		Maximum TOF _d ^{chem} (s ⁻¹) x 10 ²	% Hydrocarbon Selectivity at SS ^{b, c, e}					% Olefin ^{b,c} (C ₂ -C ₄ fraction)	□□ ^{b, c} (C ₃ -C ₆)
	CO ₂	total HC	CO ₂	total HC		C ₁	C ₂	C ₃	C ₄	C ₅ -C ₈		
100Fe	0.50	0.78	0.13	0.43	0.53	27	29	23	16	5	74	0.35
97Fe3Cr	0.96	1.34	0.23	0.50	0.62	29	28	25	13	6	74	0.35
95Fe5Cr	1.14	1.59	0.25	0.52	0.59	29	26	25	13	8	75	0.36
93Fe7Cr	1.18	1.56	0.24	0.50	0.69	28	26	25	13	8	75	0.37
90Fe10Cr	0.87	1.26	0.16	0.36	0.66	26	28	31	12	4	77	0.36
95Fe5Mn	0.99	1.58	0.24	0.72	0.83	29	26	22	18	6	82	0.35
93Fe7Mn	1.10	1.64	0.28	0.73	0.88	29	25	21	18	6	83	0.33
90Fe10Mn	1.24	1.73	0.30	0.76	0.97	32	26	22	18	2	81	0.35
80Fe20Mn	1.28	1.78	0.35	0.80	1.09	34	26	22	16	2	83	0.33
97Fe3Zr	1.01	1.35	0.20	0.53	0.79	27	26	21	19	6	78	0.34
95Fe5Zr	1.27	1.77	0.24	0.57	0.90	28	26	23	21	2	81	0.32
90Fe10Zr	1.75	2.24	0.32	0.58	1.04	31	27	24	12	6	82	0.34
86Fe14Zr	2.07	2.05	0.28	0.55	0.94	29	25	21	19	5	85	0.35

^a All catalysts also contain 5Cu and 17Si.

^b Max error = $\pm 5\%$.

^c At steady-state rate (5 h TOS).

^d Calculated from $\text{TOF}_{\text{chem}} = \text{reaction rate (at the maximum activity)} / (2 \times \text{total CO chemisorbed})$. Max error = $\pm 10\%$.

^e Based on atomic carbon.

A summary of reaction rates, TOF_{chem} s, %hydrocarbon selectivities in a carbon basis, %C₂-C₄ olefin (ethylene, propylene, and butene) selectivities, and chain growth probabilities (\square) of the various Fe-based catalysts are shown in Table 2. The TOF_{chem} values of Fe catalysts with Mn or Zr promotion increased in general with increasing their concentration while it was observed to be relatively constant for the Cr-promoted Fe catalysts. %Selectivity to hydrocarbons and \square (ca. 0.32-0.37) were similar for all catalysts, regardless of third metal %loading or type of added *Me*, within experimental error. The selectivity for olefins in the C₂-C₄ formation was improved slightly by the addition of Mn and Zr.

Comparisons of CO hydrogenation and WGS activities with %Fe dispersion for various Fe-based catalysts at different %third metal loadings and type of third metal are shown in Fig. 4. 95Fe5Cr exhibited, for the FeCr catalysts, the highest activities for both CO hydrogenation and the WGS reaction, meaning that adding Cr at 5 atomic% was the optimum concentration. The optimum %loadings of Mn and Zr were at 20 and 10 atomic%, respectively (i.e., hydrocarbon production rate of 86Fe14Zr was slightly lower than that of 90Fe10Zr). Fig. 4 also shows that initial rates for CO hydrogenation and the WGS reaction appeared to be directly related to the amount of surface exposed Fe sites chemisorbing CO (%Fe dispersion).

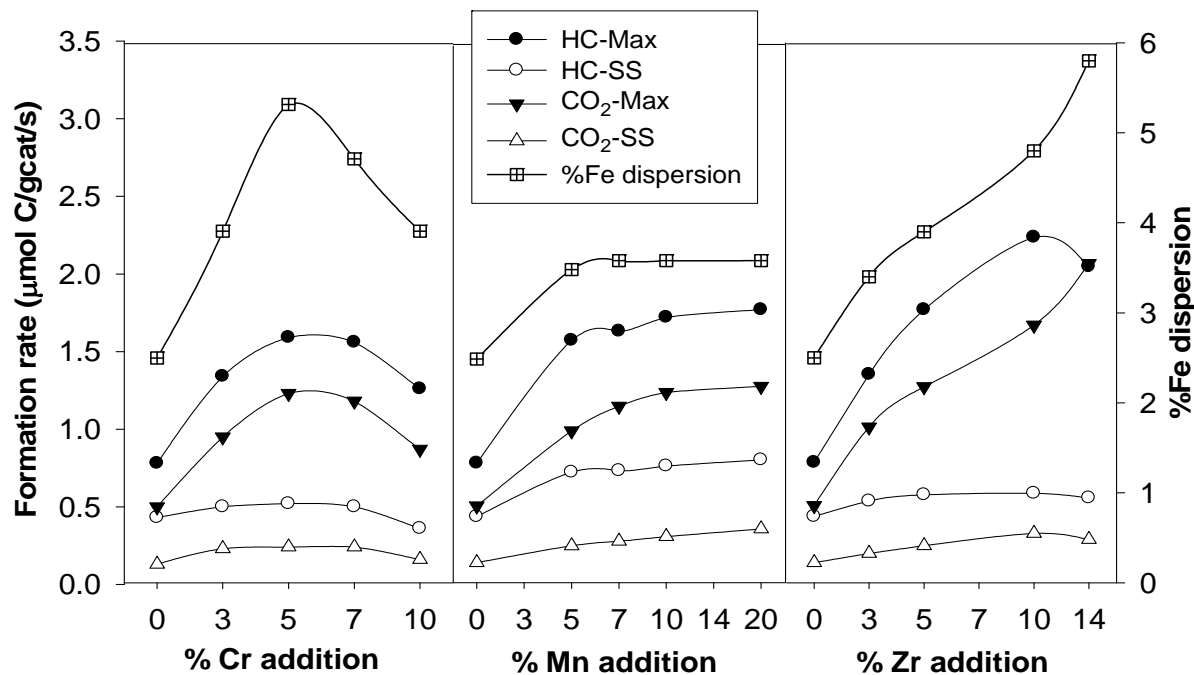


Figure 4: Comparisons of the total hydrocarbon (C₁-C₈) and CO₂ formation rate at the maximum (15 min) and steady state (5 h) activities with %Fe dispersion for various Fe-based catalysts.

The activities of FeMe at the optimum concentration of added metal (e.g., 95Fe5Cr, 80Fe20Mn and 90Fe10Zr) are re-plotted for comparison purposes and are shown in Fig. 5. 90Fe10Zr initially exhibited the highest activities for CO hydrogenation and the WGS reaction but the catalyst rapidly deactivated and became less active at long TOS. On the contrary, 80Fe20Mn was the most active and stable catalyst overall. Jensen and Massoth [6] have suggested that the promoting effect of Mn on the activity of Fe catalysts may be due to the ability of Mn oxide to modify the electronic state of Fe by being an electron donor as alkali metals do. However, Herranz et al. [7] have proposed that active carbonaceous intermediate species evolving into Hägg carbide (\square -Fe_{2.5}C) is stabilized by the presence of Mn.

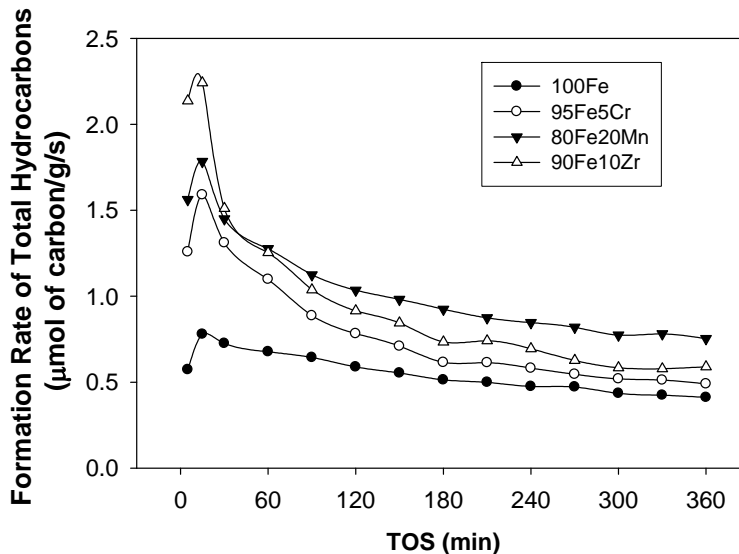


Figure 5 (a): Catalyst activities for CO hydrogenation and at the optimum concentrations of added Cr, Mn, and Zr.

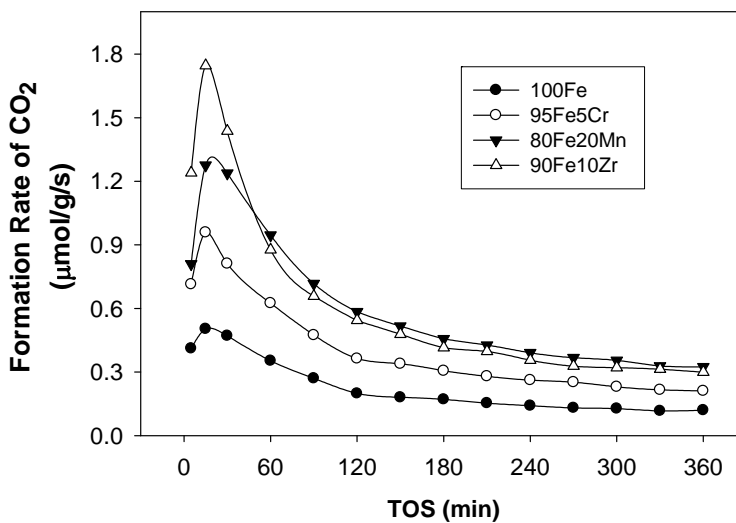


Figure 5 (b): Catalyst activities for WGS at the optimum concentrations of added Cr, Mn, and Zr.

TPR profiles of Fe catalysts with the addition of Cr, Mn and Zr are shown in Figs. 6 (a), (b), and (c), respectively. No significant difference in the reduction behavior was detected among Fe catalysts with and without third metal promotion. All the catalysts showed similar reduction peaks as those of a pure Fe_2O_3 powder but at lower reduction temperatures due to the presence of Cu (i.e., Cu is well known to facilitate the reduction of Fe [8-10]). Two distinct reduction peaks at around 215-280°C and 605°C were observed and are assigned to the reduction of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ and $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$, respectively [11, 12]. It is not a straightforward calculation to obtain an absolute value of %Fe reducibility for a complicated catalyst system containing multiple metals. However, it is likely that some Fe_2O_3 could have been reduced to Fe_3O_4 and then rapidly to Fe with the presence of Cu. Thus, the calculation of %reducibility of Fe was based on an assumption of only Fe_2O_3 reduced to Fe.

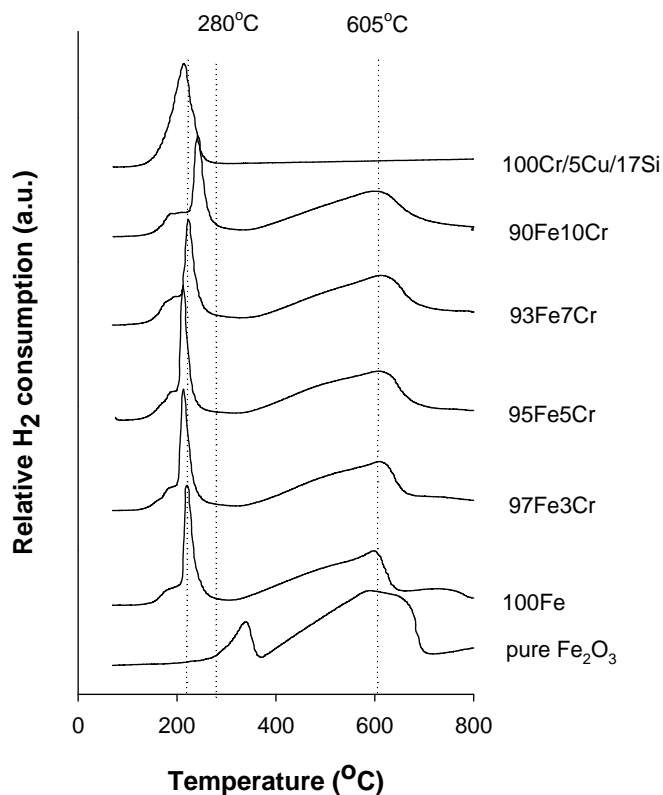


Figure 6 (a): TPR profiles of the fresh calcined FeCr catalysts at various %Cr loadings.

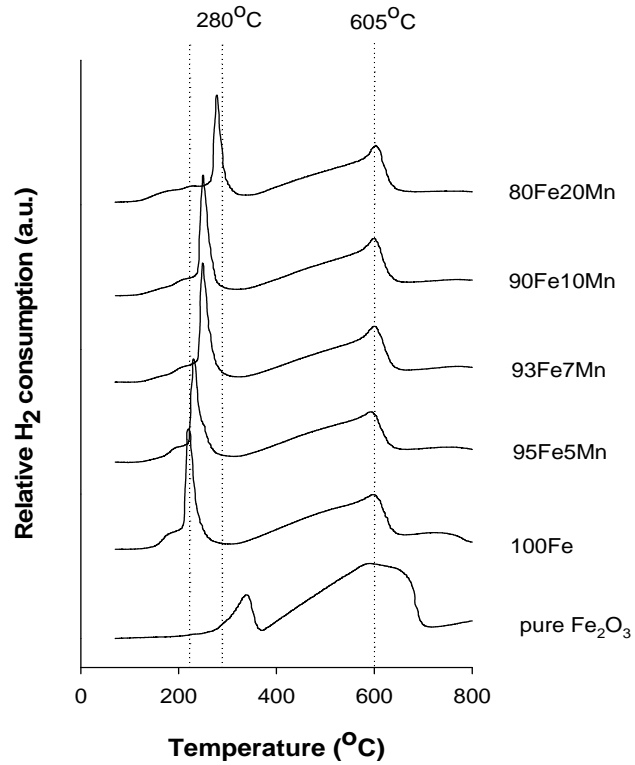


Figure 6 (b): TPR profiles of the fresh calcined FeMn catalysts at various %Mn loadings

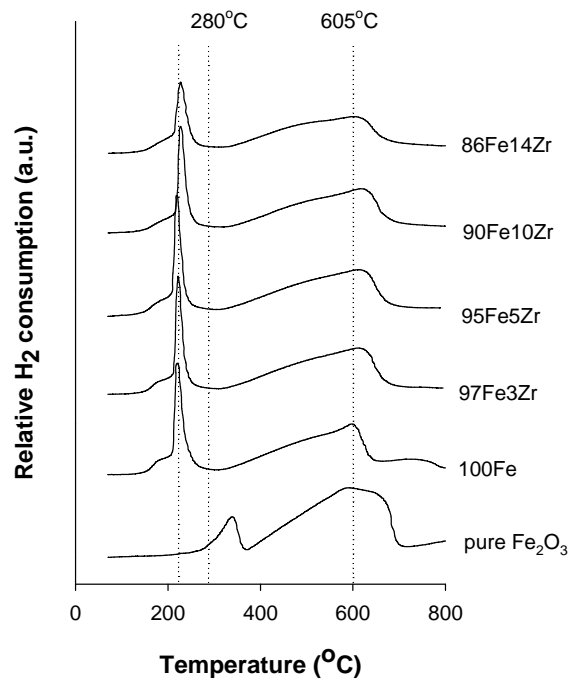


Figure 6 (c): TPR profiles of the fresh calcined FeZr catalysts at various %Zr loadings.

Previous work [13] showed that only reduction equivalent to the first reduction peak of Fe was obtained during standard reduction conditions (i.e., ramping to 280°C at 2°C/min and holding for 12h) used prior to reaction. Therefore, reducibility results reported in Table 3 include only those determined from the first reduction peak. It was found that %reducibility of Fe was in the range of 32-39% and was affected by neither type of added metal nor its concentration. However, reduction peak temperatures did vary slightly among the catalysts depending upon type of added metal and its concentration. For example, a reduction peak temperature of the FeCr catalysts shifted to higher values and a small shoulder peak at ~210°C became more noticeable with increasing %Cr loading [Fig. 6 (a)]. Comparing the small shoulder peak at 210°C of 90Fe10Cr with a reduction peak temperature of a 100Cr/5Cu/17Si sample [no Fe present, see Fig. 6 (a)] at 215°C, it appears likely that the presence of this small shoulder peak was due to the reduction of Cr₂O₃ [14].

Table 3: Results from TPR and CO-Chemisorption for the various Fe catalysts.

Catalyst ^a	H ₂ -TPR (1 st peak)	
	Peak temperature (°C) ^b	%Fe Reducibility ^c
100Fe	220	35
97Fe3Cr	213	35
95Fe5Cr	212	39
93Fe7Cr	222	41
90Fe10Cr	242	39
95Fe5Mn	241	33
93Fe7Mn	249	34
90Fe10Mn	251	36
80Fe20Mn	278	32
97Fe3Zr	222	34
95Fe5Zr	217	37
90Fe10Zr	229	36
86Fe14Zr	227	35

^a All catalysts also contain 5Cu and 17Si.

^b Max error = ± 2%.

^c %Fe reduced in 1st TPR peak. Equivalent to %Fe reduced during standard reduction.
Max error = ± 5%.

A shift of the first reduction peak to higher temperatures was also observed for the Mn-promoted Fe catalysts [Fig. 6 (b)]. This apparently suggests that Fe was harder to reduce in the presence of Mn which may be due to the ability of MnO to stabilize Fe²⁺ [6, 15, 16]. The existence of mixed oxide phases between Fe₃O₄ and Mn₃O₄ has been reported for FeMn catalyst

(without Cu or Si present) and has been suggested to inhibit the migration of Fe cations to the surface of catalyst during reduction, causing Fe to be less reduced [6]. On the other hand, the reduction process of Fe was not influenced by the addition of Zr. Relatively the same %Fe reducibilities and reduction temperatures were observed for all Zr-promoted Fe catalysts.

3.0 Conclusions

The addition of Cr, Mn, and Zr was shown to increase the activities of a precipitated FeCuSiO₂ catalyst for both CO hydrogenation and WGS activity and to promote the dispersion of Fe. However, % Fe reducibility, %hydrocarbon selectivity and the chain growth probability (□ □ were not altered by the presence of the third metal or its concentration.

4.0 Next Quarter's Activities

Research carried out in the next quarter will be an investigation of the impact of Cr, Mn, Zr and K addition to the Fe catalyst (shown to exhibit the highest activities) on surface kinetic parameters determined using SSITKA (steady state isotopic transient kinetic analysis). Analysis of EXAFS results for these catalysts will be completed. If contracts issues can be sorted out, it is hoped that CSTR reaction studies of the most active catalysts can be begun.

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