



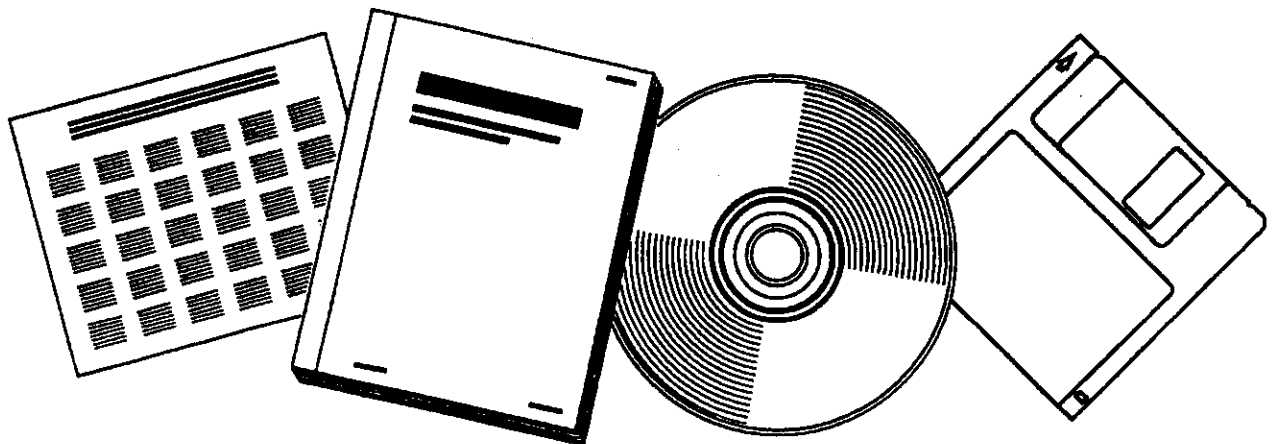
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**IMPROVED FISCHER-TROPSCH SYNTHESIS
CATALYSTS FOR INDIRECT COAL LIQUEFACTION:
QUARTERLY TECHNICAL PROGRESS REPORT NO. 5
FOR THE PERIOD 1 OCTOBER TO 31 DECEMBER
1986**

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IMPROVED FISCHER-TROPSCH SYNTHESIS CATALYSTS
FOR INDIRECT COAL LIQUEFACTION

By: G. T. Tong, R. B. Wilson, and J. G. McCarty

Prepared for:

UNITED STATES DEPARTMENT OF ENERGY
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, Pennsylvania 15236-0940

Attention: Edgar B. Klunder, Project Manager

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Approved:

D. L. Hildenbrand
D. L. Hildenbrand, Director
Materials Research Laboratory

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333 Ravenswood Ave. • Menlo Park, CA 94025
415-326-6200 • TWX: 910-373-2046 • Telex: 334-486

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SUMMARY

Surface-confined ruthenium cluster catalysts have been prepared with alumina, Y-zeolite, and molecular sieve supports. The Al-Ru₄ and Al-Ru₆ hydridocarbonyl cluster complexes previously used to prepare alumina-supported cluster catalysts were used in similar surface-confining reactions with sodium Y-zeolite and molecular sieve zeolite supports. Infrared (FTIR) spectra, gas evolution, and elemental analysis were used to follow the surface-confining reaction. In all cases, the confined complexes of Al-Ru₄ and Al-Ru₆ had the composition $-O-Al(C_2H_5)[(H)Ru_4(CO)_{12}]$ and $-O-Al(C_2H_5)[(H)Ru_6(CO)_{18}]$, respectively. Monomeric ruthenium catalysts have also been prepared for all three supports by surface confining reactions with the complex $(allyl)_2Ru(CO)_2$.

The support material has been shown to alter the inherent activity and selectivity of ruthenium Fischer-Tropsch synthesis (FTS) catalysts, and it may affect the stability of the ruthenium clusters during activation and FTS reaction. The series of Ru cluster catalysts ranges from one, four, and six atoms confined on surfaces of three supports with variable acidity and porosity, beta alumina, sodium Y-zeolite, and molecular sieve zeolite. These catalysts will be tested for FTS activity and selectivity for syn gas with $H_2/CO = 1.0$ at 1 atm using a hot wax trap to determine if a catalyst shows a decline in the Schultz-Flory Anderson product distribution above decane.

A potassium and copper doubly-promoted precipitated iron catalyst was prepared for evaluation of the effect of sulfur treatment on the methane selectivity and olefin-to-paraffin ratio of light hydrocarbons. Lack of reproducible surface area after reduction and the difficulty of measuring metal surface areas complicated efforts to synthesize this catalyst with low sulfur coverage. The FTS activity and methane selectivity of the precipitation iron catalyst were inferior to those of the standard fused iron catalyst, and high-level sulfur treatment

resulted in a catalyst with much greater activity and much less suppression of methane than previously obtained by similar treatment of the fused iron catalyst. Additional precipitated and supported iron and supported cobalt FTS catalysts will be stabilized and sulfur-treated at roughly half monolayer coverage in an effort to find a catalyst with properties superior to the low-level sulfur-treated fused iron catalyst.

EXPERIMENTAL RESULTS

Task 1: Synthesis of Dual-Function Mixed-Metal Cluster Catalysts

Surface-confined Fischer-Tropsch synthesis (FTS) catalysts are being synthesized in Task 1, using a pendant hydrocarbyl functional group that reacts with hydroxyl groups on the surface of an appropriate support material. This work is divided into the following subtasks:

- A. Synthesis of hydridocarbonyl ruthenium clusters.
- B. Reaction of hydridocarbonyl clusters with alkyl aluminum to give alkyl aluminum carbonyl ruthenium clusters.
- C. Reaction of alkyl aluminum carbonyl ruthenium clusters with the support.
- D. Synthesis of alkyl complexes of Fe, Ru, and Co.
- E. Reaction of alkyl complexes with the support.
- F. Reaction of alkyl complexes with hydridocarbonyl ruthenium clusters to give alkylcarbonyl clusters.
- G. Reaction of alkylcarbonyl clusters with the support.
- H. Synthesis of mixed-metal (Fe, Ru) hydridocarbonyl clusters.
- I. Reaction of mixed-metal hydridocarbonyl clusters with alkyl aluminum to give alkyl aluminum mixed-metal carbonyl clusters.
- J. Reaction of alkyl aluminum mixed-metal carbonyl clusters with the support.
- K. Reaction of mixed-metal hydridocarbonyl clusters with alkyl complexes to give alkyl mixed-metal carbonyl clusters.
- L. Reaction of alkyl mixed-metal carbonyl clusters with the support.

During the fourth quarter of 1986, progress was made in subtasks C and E of Task 1. A description of these subtasks and the progress to date follows.

Task 1C: Reaction of Alkyl Aluminum Carbonyl Ruthenium Clusters with the Support. In the previous quarterly report, we described in detail the synthesis and characterization of two hydridocarbonyl multiatomic ruthenium cluster complexes, $(H)_4Ru_4(CO)_{12}$ and $(H)_2Ru_6(CO)_{18}$. The FTIR spectra of these complexes in solution showed several CO stretching frequencies, and their proton NMR spectra showed singlet peaks, indicating that the solutions were pure and that the clusters had the structure expected from reports in the literature. Ethyl aluminum ruthenium hydridocarbonyl clusters were synthesized from the Ru_4 and Ru_6 clusters by reaction of triethyl aluminum in tetrahydrofuran (THF) overnight at 25°C. Measurement of the amount of ethane evolved by the synthesis indicated that the compositions of the Al- Ru_4 and Al- Ru_6 clusters were $(Et_2Al)Ru_4(H)_3(CO)_{12}$ and $(Et_2Al)Ru_6(H)(CO)_{18}$, respectively. The FTIR and NMR spectra (Table 1) of the Al-Ru clusters were complex, but consistent with the above formulations.

Four new supported multiatomic ruthenium cluster catalysts were prepared by reaction of the Al- Ru_4 and Al- Ru_6 complexes with a sodium Y-zeolite (Union Carbide LZ-Y52) and a molecular sieve zeolite (Union Carbide 5A). The method of preparation was the same as described previously for the β -alumina supported Ru_4 and Ru_6 cluster catalysts, the facile reaction in THF at 25°C of the Al-Ru complexes with Bronsted acid sites on the support surfaces. The Bronsted acid site density was determined by titration with ethyl lithium. Excess hydroxyl groups were available for reaction with the clusters since the metal loading was a few weight percent. The stoichiometries of the surface-confining reaction of the clusters with the supports were again determined by measuring the amount of ethane evolved during the surface-confining reaction. No carbon monoxide was released, and only one equivalent of ethane was produced with respect to the ruthenium cluster used.

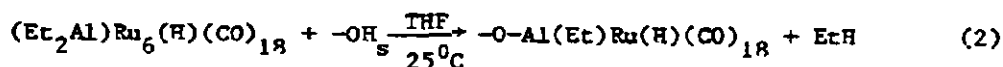
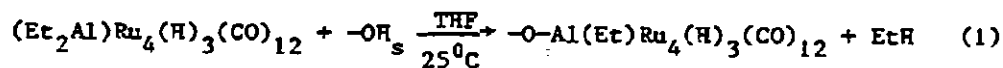


Table 1

FTIR AND NMR SPECTRA OF RUTHENIUM HYDRIDOCARBONYL CLUSTERS

Cluster	FTIR bands (cm ⁻¹) ^a	NMR peaks (ppm) ^b
H ₄ Ru ₄ (CO) ₁₂	2081(s), 2067(s), 2024(s), 2030(m)	-17.9 (sgl)
H ₂ Ru ₆ (CO) ₁₈	2058(s), 2052(s) 2003(w)	+8.8 (sgl)
C ₂ H ₅) ₂ AlRu ₄ (H) ₃ (CO) ₁₂	2016(s), 1998(s), 2037(m), 2030(m), 1976(m)	5.22 (sgl) 4.17 (dbl) 2.01 (tpl)
(C ₂ H ₅) ₂ AlRu ₆ (H)(CO) ₁₈	2059(s), 2025(s), 1993(s), 2044(m), 1972(m), 1960(m), 1947(m)	5.78 (sgl)

^a (s), (m), (w) qualitatively refer to strong, moderate, and weak intensity in the FTIR spectra.

^b (sgl), (dbl), (tpl), refer to singlet, AB doublet, and triplet peaks, respectively, in C₆D₆ solvent.

Elemental analyses of the tetraruthenium cluster and hexaruthenium cluster catalysts on all the supports were performed by a commercial analytical laboratory (Galbraith Laboratory). The results (Table 2) showed that the ruthenium loadings ranged from 0.2 wt% for Ru₆/Na Y-zeolite to 1.26 wt% for Ru₆/β-alumina.

Task 1E: Reaction of Alkyl Complexes with the Support. Monomeric ruthenium cluster catalysts were prepared for all three support materials by reaction with (allyl)₂Ru(CO)₂ in THF solution at 25°C. The synthesis of the allyl ruthenium complex was described in the previous quarterly report. Evolved gas product (e.g., propylene, propane, carbon monoxide) could not be detected by gas chromatography for reaction with β-alumina. Therefore, the metal complex may have simply absorbed on the support or the alkyl may have been released in the form of alcohol.

Task 2: Sulfur Treatment of Fisher-Tropsch Catalysts

Catalyst Preparation—A doubly promoted (potassium and copper) precipitated iron catalyst was prepared from aqueous solutions of copper (II) nitrate (Cu(NO₃)₂·3H₂O, Alfa Products, puratronic grade) and iron (III) nitrate (Fe(NO₃)₃·9H₂O, Alfa Products, puratronic grade) in the required ratio at 353 K. The mixed nitrate solution was then slowly added to hot sodium carbonate solution with vigorous stirring over several minutes until the pH reached 7 to 8. The precipitate was collected by centrifugation and washed with 1000 ml deionized water. Alkali was added by stirring the precipitate with dilute potassium carbonate solution. The catalyst was then dried at 373 K for 24 hours. The final weight ratio was Fe:Cu:K₂CO₃ = 100:0.1:2.

The precipitated iron catalyst was ground and screened to a powder of 0.043–0.014 mm. The catalyst was reduced in situ in the FTS catalytic reactor at 623 K for 16 hours with hydrogen gas at a flow gas hourly space velocity (GHSV) of 3 x 10⁴ h⁻¹.

Table 2

ELEMENTAL ANALYSIS OF SUPPORTED RUTHENIUM
CLUSTER CATALYSTS

Cluster	Support	Analysis (wt%)	
		Ru	C
Ru ₄	β -Al ₂ O ₃	0.61	5.09
Ru ₄	Na Y-zeolite	0.51	5.25
Ru ₄	5A mol. sieve	0.49	1.46
Ru ₆	β -Al ₂ O ₃	1.26	9.77
Ru ₆	Na Y-zeolite	0.20	8.07
Ru ₆	5A mol. sieve	0.19	0.95

Sulfur Treatment of the Precipitated Iron Catalyst—Sulfur treatment of the precipitated iron catalyst was performed in a gas recirculation system, as described previously. After catalyst reduction in situ in 1-atm H_2 at 623 K for 16 hours, aliquots of 0.96% H_2S/H_2 were injected into the recirculation loop at 723 K and the change in gas phase concentration of hydrogen sulfide with time was closely monitored. Approximately 39.3 μmol of hydrogen sulfide was adsorbed at saturation, corresponding to a reduced metal surface area of about $6.7 \text{ m}^2/\text{g}$.

The catalyst was exposed to the gaseous mixture for 24 hours at 723 K to ensure equilibration. The H_2S gas was then flushed with pure hydrogen after cooling to 423 K. Sulfur chemisorption isosteres were determined (Figure 1) by measuring the gas-phase hydrogen sulfide concentrations over a range of temperatures. Comparison with our previously published isosteres for iron powder¹ indicates that the ppt iron catalyst had reached approximately 100% of saturation coverage (i.e., about 1.0 sulfur addition per iron surface atom). The catalyst was then removed from the recirculation system and immediately reduced at 623 K with 1-atm H_2 in the FTS testing apparatus.

Task 3: Characterization and Testing of FTS Catalysts

Surface Area Measurement—We used nitrogen BET adsorption to determine the surface areas of the precipitated and fused iron catalysts before and after reduction, before and after sulfur treatment, and before and after Fischer-Tropsch synthesis. Table 3 summarizes the surface areas of various catalysts tested for FTS reactivity during the current and previous quarters. The variability of surface area of the precipitated iron catalyst following reduction and sulfur treatment is of great concern because it seriously limits the ability to prepare partially sulfur-covered catalysts.

FTS Test Results—All iron catalysts tested for Fischer-Tropsch synthesis activity were reduced in situ in the characterization and FTS testing apparatus in $1.7 \text{ cm}^3\text{s}^{-1}$ of flowing hydrogen at 623 K for 2 hours. The reactor was then cooled before switching to the hydrogen-carbon

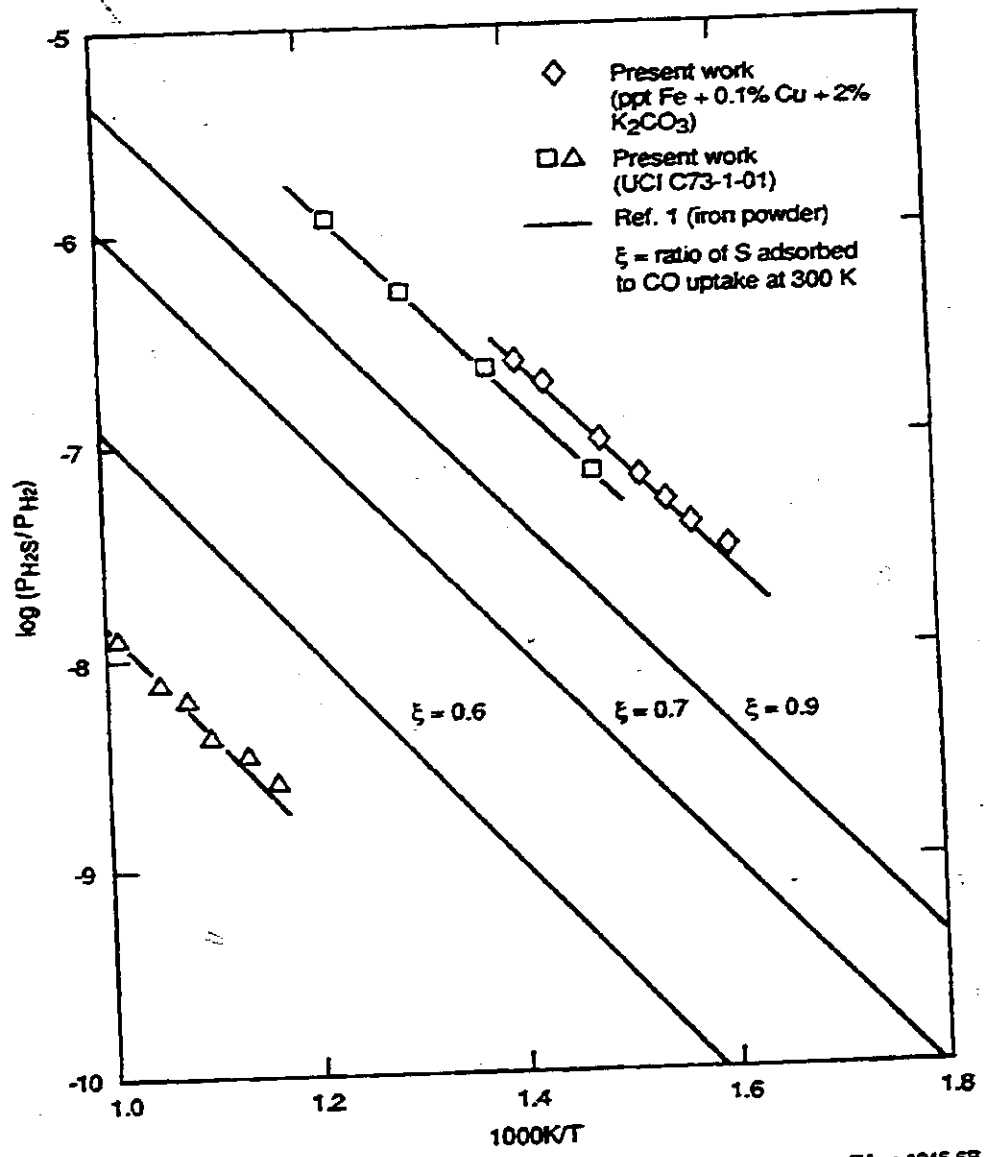


FIGURE 1 SULFUR CHEMISORPTION ISOTHERES ON FUSED
 IRON, PRECIPITATED IRON AND IRON POWDER

Table 3
N₂ BET SURFACE AREA MEASUREMENT

Catalyst	Sample No. ^a	Reduction ^b	Sulfur Treatment	Surface Area (m ² /g)
Fused Fe	—	After	No	31
Fused Fe	—	After	Yes ($\theta_s = 0.9$)	—
Fused Fe	—	After	Yes ($\theta_s = 0.4$)	—
ppt Fe + 0.1% Cu + 2% K	1	Before	No	47
ppt Fe + 0.1% Cu + 2% K	1	After (30.4% wt loss)	No	16
ppt Fe + 0.1% Cu + 2% K	2	Before	No	43
ppt Fe + 0.1% Cu + 2% K	2	After (25.5% wt loss)	No	11
ppt Fe + 0.1% Cu + 2% K	2	After (25.5% wt loss)	Yes ($\theta_s = 1.0$)	2

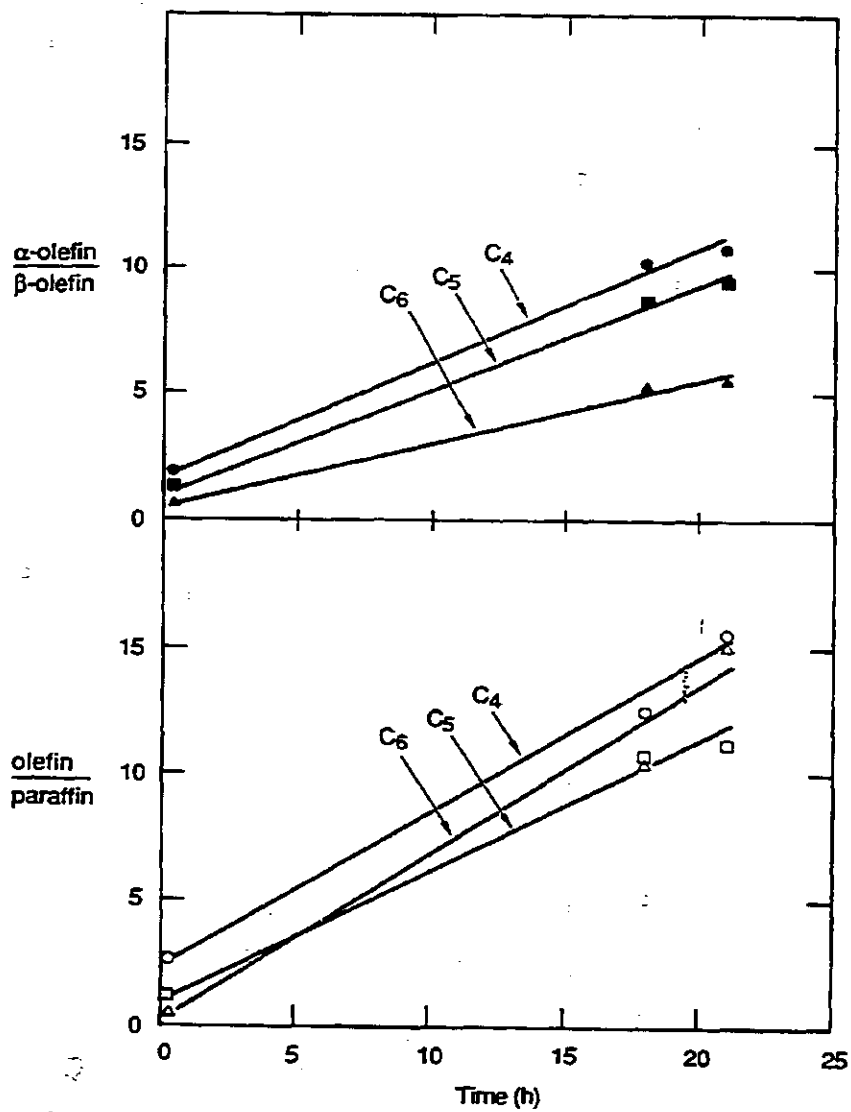
^aSamples 1 and 2 for the ppt iron catalyst were taken from the <0.043 mm and <0.074 mm screened powders, respectively.

^bReduction in H₂, 298 K to 623 K, at 0.033 cm³s⁻¹ for 16 h.

monoxide mixture. Typically, 0.2 to 0.5 g of catalyst was used. The Fischer-Tropsch synthesis reaction was conducted with 1-atm synthesis gas of fixed composition ($H_2/CO = 2.1$) at 573 K for the precipitated iron catalysts. The FTS reaction for the fused iron catalyst was conducted at 548 K and compared with previous runs at 573 K. A gas hourly space velocity GHSV between 4×10^3 and $1 \times 10^4 \text{ h}^{-1}$ was used to achieve differential reactor conditions depending on the catalyst's activity.

An auxiliary subambient control system was installed in our wide-bore capillary flame ionization gas chromatograph to allow separation of light olefins and paraffins while retaining the capacity to determine hydrocarbons through C_{16} . The new GC configuration was calibrated and used for FTS testing of the Ru cluster catalysts and precipitated iron catalysts. The Fischer-Tropsch synthesis experiments (Table 4), were conducted under differential conditions with a maximum CO conversion of 5%. The hydrocarbon rate (R) is defined here as the number of nanomoles of carbon monoxide converted to C_1 through C_8 hydrocarbons per gram of catalyst per second. The selectivity (S) is defined as the ratio of the rate of formation of C_1 through C_8 products (on a carbon mole basis) to the overall hydrocarbon reaction rate.

Both the clean fused iron and precipitated iron catalysts exhibited high initial Fischer-Tropsch synthesis (FTS) and water gas shift (WGS) activities. The amount of methane and carbon dioxide in the product decreased with time on stream. The activity of the fused iron catalyst could be restored to its original value by temperature programmed reaction (TPR) in 1-atm hydrogen up to 773 K following a 24-hour synthesis run. Initially, the clean fused iron catalyst produced hydrocarbons with a chain growth probability factor, α , of 0.52 and a methane selectivity of 21%. The initial olefinic content of higher hydrocarbon products was low, but increased with time on stream (Figure 2). The ratio of α -olefin to β -olefin was lower for increasing carbon number and increased also (Figure 2) with time on stream. Satterfield and Haulon² observed similar initial behavior on a reduced fused-magnetite catalyst. After 24 hours of synthesis reaction, the



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FIGURE 2 OLEFIN SELECTIVITIES FOR POTASSIUM-PROMOTED FUSED IRON CATALYST
 $\text{H}_2:\text{CO} = 2:1$, 548K, GHSV = 1300 h^{-1}

catalyst was 30% selective toward methane with a slight decrease in chain growth factor. These results (Table 4) are consistent with earlier FTS experiments at 573 K, although the steady-state activity is lower than expected.

The clean precipitated iron catalyst initially produced hydrocarbons with 24% methane selectivity and a chain growth probability factor of 0.50. In contrast to the fused iron catalyst, the initial olefinic content of higher hydrocarbon products for the precipitated iron catalyst was high, but decreased with time on stream. Unlike the fused iron catalyst, the precipitated iron catalyst was 68% selective toward methane, with an inexplicably large decrease of α to 0.25 after 17 hours of synthesis reaction. The sulfur-treated precipitated iron catalyst had low initial FTS activity with a threefold reduction after 20 hours, but the selectivity toward methane remained constant at about 50%.

Table 4

FIS TEST RESULTS

Catalyst	Temp. (K)	Duration (h)	Hydrocarbon Product Rate ^a (mmol ⁻¹ g cat ⁻¹ h ⁻¹)					C ₇	C ₈	Total (C atom base)	α^b	β^c	Methane Selectivity ^d	
			C ₁	C ₂	C ₃	C ₄	C ₅							C ₆
Tuned Fe (clean)	548	24	11.21	5.20	2.86	1.24	0.51	0.23	0.14	0.08	40.7	0.50	15	30
Tuned Fe ^e (clean)	573	22	57.8	24.1	5.37	2.46	1.19	0.52	0.26	--	139.2	0.47	--	42
Tuned Fe ^e + sulfur ($\theta_s = 0.9$)	573	20	0.24	0.72	0.13	0.055	0.017	0.006	--	--	2.4	0.36	>20	18
ppt Fe + 0.1 wt% Cu + 2 wt% K ₂ CO ₃ (clean)	573	17	9.46	1.48	0.54	0.11	0.02	--	--	--	14.6 ^f	0.25	2.5	68
ppt Fe + 0.1 wt% Cu + 2 wt% K ₂ CO ₃ + sulfur ($\theta_s = 1.0$)	573	20	0.52	0.20	0.08	0.01	--	--	--	--	1.28	0.21	--	48

^an-Paraffin and α -, β -olefins) total = total moles carbon converted into hydrocarbons.

^bChain growth probability factor.

^cAverage olefin to paraffin ratio for C₂-C₅ fraction.

^dC₁ rate/(total rate) x 100%.

^eFrom previous quarterly report.

^fC₁-C₅ fraction.

^gC₁-C₄ fraction.

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DISCUSSION

Surface Area of Precipitated Iron FTS Catalysts

CO adsorption measurements have been performed in our laboratory in addition to BET adsorption to estimate the metal surface areas of promoted fused iron and precipitated iron catalysts. Adsorption at 300 K resulted in estimates of metal surface areas less than $1 \text{ m}^2/\text{g}$. Recent studies by Rankin and Bartholomew³ revealed that both CO and H₂ adsorption were impeded by the addition of potassium to a supported iron catalyst. A tenfold reduction of CO adsorption capacity was observed with the addition of 3 wt% potassium. Such blockage of adsorption sites was attributed to the presence of potassium oxide or a "potassium-support complex" on the iron surface. Fifty years ago, Emmett and Brunauer⁴ reported that CO adsorption capacity of unsupported iron decreased with addition of potassium due to the presence of K₂O (in precipitated iron) or K₂O(SiO₂)₂ (in fused iron) on the surface. Dry⁵ observed that K₂O does not dissolve in solid iron, but is present at the interface between iron particles.

CO adsorption measurements may still be possible if performed at higher temperature (473 K), as we have experienced with our recirculation gas system before sulfur treatments, although some CO disproportionation also occurs. The lack of a reliable measure of the metal surface area of promoted iron catalysts remains a difficulty in preparing fractional monolayer sulfur-treated iron FTS catalysts. As a result, another precipitated iron catalyst is being prepared in our laboratory without alkali promoters to verify the effect of potassium on CO and H₂ chemisorption and on selectivity during FTS.

Report from Sixth DOE Indirect Liquefaction Contractors' Meeting

Several of the talks at the Sixth DOE Indirect Liquefaction Contractors' meeting held in Monroeville, Pennsylvania, December 3-4, 1986, were directly related to our project.

Jim Miller of Union Carbide has been studying bifunctional catalysts that contain promoted cobalt as the FTS active component and molecular sieves to provide molecular weight control through shape selectivity. Miller et al. have been successful at producing highly active catalysts: catalysts that produce 89% C₅₊ yields with 45% CO conversion using a mysterious promoter labeled X₁₁ and zeolite TC-123. Increasing conversion to 79% decreased C₅₊ yield to 77%. These results are very promising; however, the one negative aspect is that the molecular sieve was not significantly affecting the molecular weight distribution. Miller et al. still observe Shultz-Flory-Anderson (SFA) distributions of products and thus observe significant wax production. The zeolite does appear to affect the methane yield, decreasing it by a factor of two. Cobalt particles were observed in the size range of 30 to 100 Å.

Henry Foley from American Cyanamid has been investigating the use of carbon molecular sieves for molecular weight distribution control in FTS. Foley is pursuing two directions. The first is encapsulation of the FTS catalyst in a coating prepared from the carbon molecular sieve material to control diffusion of reactants to the catalyst and products away from the catalyst. The second direction is synthesis of FTS catalysts within the pores of carbon molecular sieves, similar to the techniques used for zeolites. Both approaches have proved rather disappointing.

Howard Withers, of Air Products, is looking at cobalt carbonyl supported on zirconia. He has observed no deviation from the SFA distribution.

The work of G. Abrevaya of Allied Signal Research Center (UOP) is most closely related to our objectives. He is studying the effect of metal particle size of ruthenium catalysts on the product distribution.

Abrevaya reported that small ruthenium metal particles apparently did not reduce wax formation, but may significantly reduce the production of light hydrocarbons. However, he also found that ruthenium particles supported by Y-type zeolites are stable and highly active.

The conclusion from these presentations is that that previous reports in the literature of non-SFA product distributions, observed over very small particles or with catalysts having small pore volumes, appear to be experimental artifacts. Our current work with the cluster catalysts directly addresses this question.

Professor C. N. Satterfield, of MIT, reported that the hydrocarbon product distribution beyond about C_4 was not significantly altered by temperature over a range from 500 K to 600 K for a slurry reactor operating at 1000 psi on 1.5 H_2/CO syn gas. This conclusion stems from an examination of the Sassol data and recent MIT results and directly contrasts with numerous fixed-bed differential laboratory studies at 1 atm. The finding suggests that wax formation cannot be suppressed by increasing the slurry reactor temperature. Our approach with sulfur poisoned iron FTS catalysts is to selectively decrease CH_4 production and increase light olefin production, then restore activity and suppress wax formation by operation at elevated temperature in a fixed-bed reactor. In future work, the methane selectivity and hydrocarbon chain growth parameter of promising selective catalysts will be determined as a function of temperature in Task 4 under integral reaction conditions at higher pressure.

Recent Relevant Literature

Dave Curtis and coworkers at the University of Michigan were recently issued a patent⁶ on the use of mixed metal Mo-Fe, Mo-Co, Mo-Ni clusters for hydrogenation of CO. When these mixed metal sulfide clusters were supported on alumina, they catalyzed CO hydrogenation mostly to methane with small amounts of ethane and ethylene, but no higher hydrocarbons. R. Arakawa et al.⁷ found that using a hybrid Rh-Ti-Fe-Ir catalyst and low conversion (~ 6.2%) an in situ dehydrogenation

catalyst could change the product of CO hydrogenation from 50% ethanol to 45% ethylene (given as % of carbon converted).

Two other articles discuss the effect of particle size of ruthenium particles on CO hydrogenation. The buildup of hydrocarbon on the catalyst surface was studied by in situ IR with the finding⁸ that low dispersion catalysts gave longer chain hydrocarbons as represented by CH₂ groups. The only difference between the high and low dispersion catalysts was that the low dispersion catalyst had been calcined. A similar study⁹ showed the opposite result based on the hydrocarbons product distribution measured by gas chromatography.

TECHNICAL STATUS

The following work has been performed during the past quarter:

- Synthesized a series of Ru, Ru₄, Ru₆ cluster catalysts supported on sodium Y-zeolite, and molecular sieve zeolites.
- Characterized and tested for FTS selectivity a fresh and high-level sulfur-treated K- and Cu-promoted precipitated iron catalyst.

During the next quarterly period (January-March 1987), we expect to perform the following tasks:

- Characterize and test for FTS activity and selectivity the series of supported Ru, Ru₄, and Ru₆ cluster catalysts.
- Prepare, characterize, and test for FTS low-level sulfur-treated precipitated iron catalysts.

REFERENCES

1. J. G. McCarty and H. Wise, *J. Chem. Phys.* 76, 1162-1167 (1986).
2. C. N. Satterfield and R. T. Hanlon, *Ind. Eng. Chem. Proc. Res. Dev.* 25, 401-407 (1986).
3. J. L. Rankin and C. H. Bartholomew, *J. Catal.* 100, 533-540 (1986).
4. P. H. Emmett and S. Brunauer, *J. Amer. Chem. Soc.* 59, 310 (1937).
5. M. E. Dry, *Catalysis Science and Technology*, Vol. 1, Chapter 4, J. R. Anderson and M. Boudart, eds. (1981).
6. M. D. Curtis, J. W. Schwank, L. T. Thompson, and P. D. Williams, U.S. Patent No. 4,605,751, August 12, 1986.
7. H. Arakawa, Y. Kiyozumi, K. Suzuki, K. Takeuchi, T. Matsuzaki, Y. Sugi, T. Fukushima, and S. Matsushita, *Chem. Lett.* 1986, 1341.
8. T. Fukushima, K. Fujimoto, and H. Tominaga, *Applied Catalysis*, 14, 95 (1985).
9. Z. Z. Lin, T. Okuhara, and M. Miksono, *Chem. Lett.* 1986, 913.