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IMPROVED FISCHER-TROPSCH SYNTHESIS CATALYSTS FOR INDIRECT COAL LIQUEFACTION: QUARTERLY TECHNICAL PROGRESS REPORT NO. 6 FOR THE PERIOD 1 JANUARY TO 31 MARCH 1987

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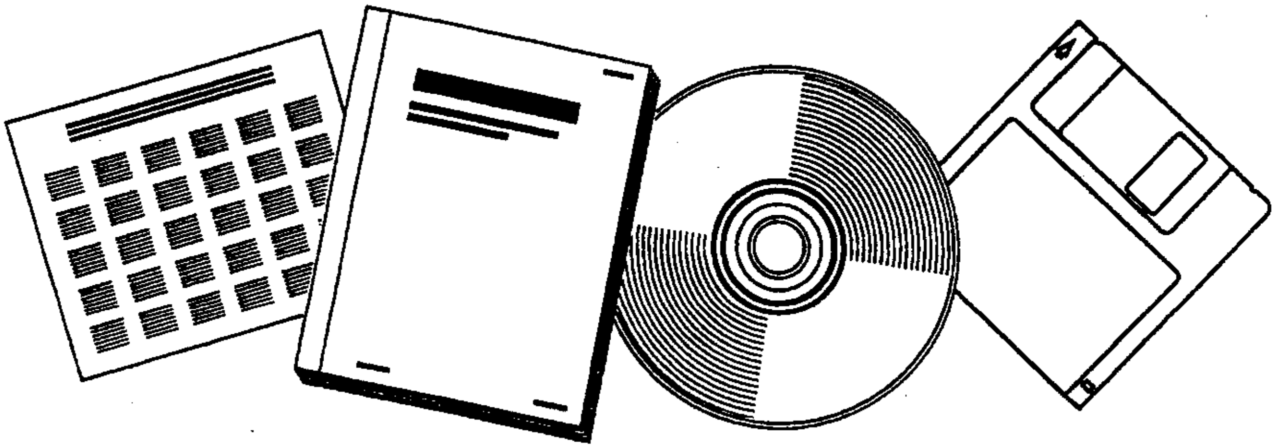

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National Technical Information Service

DOE/PC/80016-T4

DOE/PC/80016--T4

DE87 012047

June 9, 1987

Quarterly Technical Progress Report No. 6
for the Period 1 January to 31 March 1987

IMPROVED FISCHER-TROPSCH SYNTHESIS CATALYSTS FOR INDIRECT COAL LIQUEFACTION

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Contract No. DE-AC22-85PC80016
SRI Project No. 1245

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SUMMARY

Six surface-confined ruthenium cluster catalysts supported on alumina, sodium-Y zeolite, and molecular-sieve supports were tested for Fischer-Tropsch synthesis (FTS) activity and for methane and olefin-to-paraffin selectivity for syn gas with $H_2/CO = 1.0$ at 100 kPa and 523 K. The tetraruthenium cluster catalyst supported on alumina had the highest FTS activity with a methane selectivity of 61%. The hexaruthenium cluster catalyst supported on sodium-Y zeolite had the lowest methane selectivity (36%) and the highest olefin selectivity (ethylene/ethane > 20). The Schulz-Flory product distribution and chain growth factors for all ruthenium cluster catalysts through C_8 were nearly independent of support type and cluster size.

An unpromoted FTS cobalt catalyst supported on alumina was prepared to evaluate the effect of sulfur treatment on the methane selectivity and olefin-to-paraffin ratio of light hydrocarbons.

A low-level sulfur-treated fused iron catalyst (20% monolayer sulfur coverage) was prepared and tested for FTS activity and selectivity for syn gas with $H_2/CO = 1.0$ at 100 kPa and 573 K. This sulfur-treated catalyst showed almost a twofold reduction in methane yield compared with the clean fused iron catalyst. The sulfur-treated catalyst also demonstrated good stability, showing no sign of deactivation throughout a 24-h synthesis run.

Final FTS testing with sulfur-treated cobalt and the remaining ruthenium monomer catalysts will complete the screening phase of this project.

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.

Through the first quarter of 1987, progress was made in subtasks A through E of Task 1. A description of these subtasks and the progress to date follows.

Tasks 1A and 1B. We have 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 of the Al-Ru clusters were complex but consistent with the above formulations.

Task 1C. Six supported multiatomic ruthenium cluster catalysts were prepared by reaction of the Al-Ru_4 and Al-Ru_6 complexes with alpha-alumina (Kaiser), a sodium Y-zeolite (Union Carbide LZ-Y52), and a molecular-sieve zeolite (Union Carbide 5A). The method was the facile reaction of the Al-Ru complexes with Bronsted acid sites on the support surfaces in THF at 25°C. 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.

Elemental analyses of the tetraruthenium and hexaruthenium cluster catalysts on all the supports were performed by a commercial analytical laboratory (Galbraith Laboratory). The results showed that the ruthenium loadings ranged from 0.2 wt% for Ru_6/Na Y-zeolite to 1.26 wt% for Ru_6/β-alumina.

Tasks 1D and 1E. Monomeric ruthenium cluster catalysts were prepared for all three support materials by reaction with $(allyl)_2Ru(CO)_2$ in THF solution at 25°C. No gas products (e.g., propene, propane, carbon monoxide) were detected by gas chromatography for the reaction with β-alumina.

Task 2: Sulfur Treatment of Fisher-Tropsch Catalysts

Preparation of Co/Al_2O_3 Catalyst--An unpromoted cobalt catalyst was prepared from an aqueous solution of cobalt (II) nitrate $[Co(NO_3)_2 \cdot 6H_2O$, Alfa Products, puratronic grade] by the method of incipient wetness on Harshaw AL-0104 alumina (BET surface area = 88 m^2g^{-1}) and crushed and screened to 0.3-0.5 mm. The catalyst was then dried in air at 400 K for 24 hours. The final weight ratio was $Co:Al_2O_3$ = 1:10.

Low-Level Sulfur Treatment of Fused Iron Catalyst--A low-level sulfur-treated fused iron catalyst (20% monolayer sulfur coverage) was successfully prepared by the technique previously used to prepare the 50% monolayer sulfur-treated catalyst. After reduction, metal surfaces were passivated by CO adsorption, dissociation, and disproportionation to CO_2 at 473 K. Aliquots of CO were injected into a closed gas recirculation loop containing 1.5 g of the reduced fused iron catalyst while the CO/CO_2 ratio was followed with a mass spectrometer. Approximately 200 μmol of CO was injected, corresponding to approximately two monolayers of adsorbed CO. During passivation, some CO_2 evolution was observed; however, most of the CO was consumed by chemisorption.

Following passivation, aliquots of 3080 ppm H_2S/H_2 were injected into the closed recirculation loop at 473 K while the gas-phase H_2S concentration was monitored with a sensitive photoionization detector as described in the previous quarterly reports. Hydrogen sulfide (25.2 μmol) was injected into the system, representing approximately 20% of the sulfur capacity of the catalyst. The gas-phase H_2S concentration slowly fell, reaching 10 ppm after 2 hours. The system was then flushed with pure hydrogen at 473 K. The deposited carbon, iron carbide, and adsorbed CO were removed by temperature-programmed reaction (TPR) to 873 K in 1-atm flowing hydrogen. Methane was observed during the TPR and reached a maximum at 710 K. Evolution of H_2S to a level of 1 ppm was observed at 700 K and the gas was quickly readsorbed at higher temperature.

The catalyst was held at 673 K in recirculating hydrogen for 12 hours to allow local microscopic surface diffusion and equilibration. The gas-phase H_2S concentration was measured continuously. The catalyst was heated only up to 873 K to avoid sintering. The catalyst was further passivated by CO adsorption at room temperature before it was removed from the recirculation system and transferred to the FTS testing system. Part of the sulfur-treated catalyst (1 g) was reduced in flowing hydrogen at 523 K for FTS testing as described in Task 3 below. The BET surface area of the low-level sulfur-treated fused iron catalyst (17 m^2g^{-1}) showed a 20% reduction compared with the freshly reduced catalyst.

Task 3: Characterization and Testing of the FTS Catalysts

Activation of Ruthenium Cluster Catalysts--The tetraruthenium and hexaruthenium cluster catalysts supported on sodium-Y zeolite, molecular sieve, and alumina (synthesized in Task 1) were activated *in situ* in the characterization and FTS testing apparatus by temperature-programmed desorption (TPD) from 300 K to 573 K in a helium carrier gas at 0.083 Ks^{-1}. Ethene evolution was detected at approximately 433 K during the activation of these catalysts. This effect indicates additional reaction of the ruthenium carbonyl clusters with the supports. At higher temperatures, C_1 and C_3 hydrocarbons were detected, perhaps from hydrogenolysis of residues of the solvent (hexane) used during the synthesis of these catalysts.

After the FTS reaction, the ruthenium cluster catalysts were unloaded from the reactor without exposure to air and examined by infrared spectroscopy (FTIR) to identify the chemical state of adsorbed CO, and samples were sent to a commercial laboratory for elemental analysis to check for loss of ruthenium through volatilization of ruthenium carbonyls.

FTS Testing of Ru Cluster Catalysts--The Fischer-Tropsch synthesis reaction was conducted with 1-atm synthesis gas of fixed composition (H_2:CO = 1:1) at 548 K and 573 K for the clean and low-level sulfur-treated fused iron catalysts and at 523 K for the tetraruthenium and hexaruthenium catalysts on various supports. A gas hourly space velocity (GHSV) between 600 h^{-1} and 1200 h^{-1} was used to achieve differential reaction conditions, depending on the catalyst's activity. All the FTS experiments were conducted under differential conditions with a maximum CO conversion of 5%.

In general, the Ru tetramer gave better FTS catalyst performance than the monomer and the hexamer. Of the six ruthenium cluster catalysts tested, the Ru_4 supported on alumina had the highest FTS activity with a 61% selectivity toward methane (Table 1) and a chain growth probability of 0.45. However, if metal weight loadings were considered for these catalysts, both the Ru_4 and Ru_6 supported on the molecular-sieve zeolite had activities comparable to Ru_4 supported on alumina. Both had an average methane selectivity of 54%, and their chain growth probabilities were 0.46 and 0.39, respectively (see Figure 1 and Table 1). In contrast, the Ru_6 clusters supported on sodium-Y zeolite had the lowest methane selectivity (36%) and the highest olefin selectivity (ethylene/ethane > 20). For the Ru_4 and Ru_6 catalysts on alumina that had been tested for FTS activity at H_2/CO ratios of both 2 and 1, both catalysts had 50% higher hydrocarbon production rate and slightly lower chain growth probability factor under the hydrogen-rich condition. However, the methane selectivity remained the same at 62% for both H_2/CO ratios.

FTS Testing of Low-Level Sulfur-Treated Fused Iron--The additional sulfur-treated fused iron catalyst was also examined for FTS activity and product distribution. Both the clean fused iron and low-level sulfur-treated fused iron catalysts (20% monolayer sulfur coverage) had high

Table 1

FTS PERFORMANCE[a] OF RUTHENIUM CLUSTER CATALYSTS

Catalyst	Ru wt Loading (%)	Run Duration (h)	Product Rate[b] $[\mathrm{nmol(g\ cat)^{-1}s^{-1}}]$												α^c	μ^d	Methane Selectivity
			CO2	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	Total			
Ru_4/Na-Y Zeolite	0.61	16	2.96	7.63	0.994	1.044	0.392	0.138	0.066	0.033	0.017	---	---	15.77[f]	0.48	1.2	52
Ru_6/Na-Y Zeolite	0.20	20	3.68	0.78	0.158	0.27	0.104	0.012	---	---	---	---	---	2.382[g]	---	---	36
Ru_4/5Å Mol Sieve	0.49	24	2.25	6.68	0.81	0.70	0.24	0.091	0.047	0.032	0.016	0.0091	0.0074	12.605	0.46	0.77	56
Ru_6/5Å Mol Sieve	0.19	24	2.73	4.41	0.87	0.56	0.19	0.053	0.028	0.0088	0.004	---	---	9.117[f]	0.39	1.3	52
Ru_4/Al_2O_3	0.61	19	2.73	12.67	1.19	1.05	0.33	0.12	0.068	0.031	0.015	0.0053	0.0043	20.958	0.45	1.1	61
Ru_6/Al_2O_3	1.20	22	4.03	9.23	0.87	0.76	0.29	0.114	0.073	0.039	0.021	0.0073	0.0058	15.983	0.43	1.1	63

[a] Reaction conditions: $H_2/CO = 1.0$, P = 100 kPa, T = 523 K, GHSV = 600 h^{-1}.

[b] Includes n-paraffin and α-, β-olefins; total = total moles carbon converted into hydrocarbons.

[c] Mean chain growth probability factor.

[d] Average olefin-to-paraffin ratio from C_2-C_6 fraction.

[e] C rate/(total rate) x 100%.

[f] C_1-C_8 fraction.

[g] C_1-C_5 fraction.

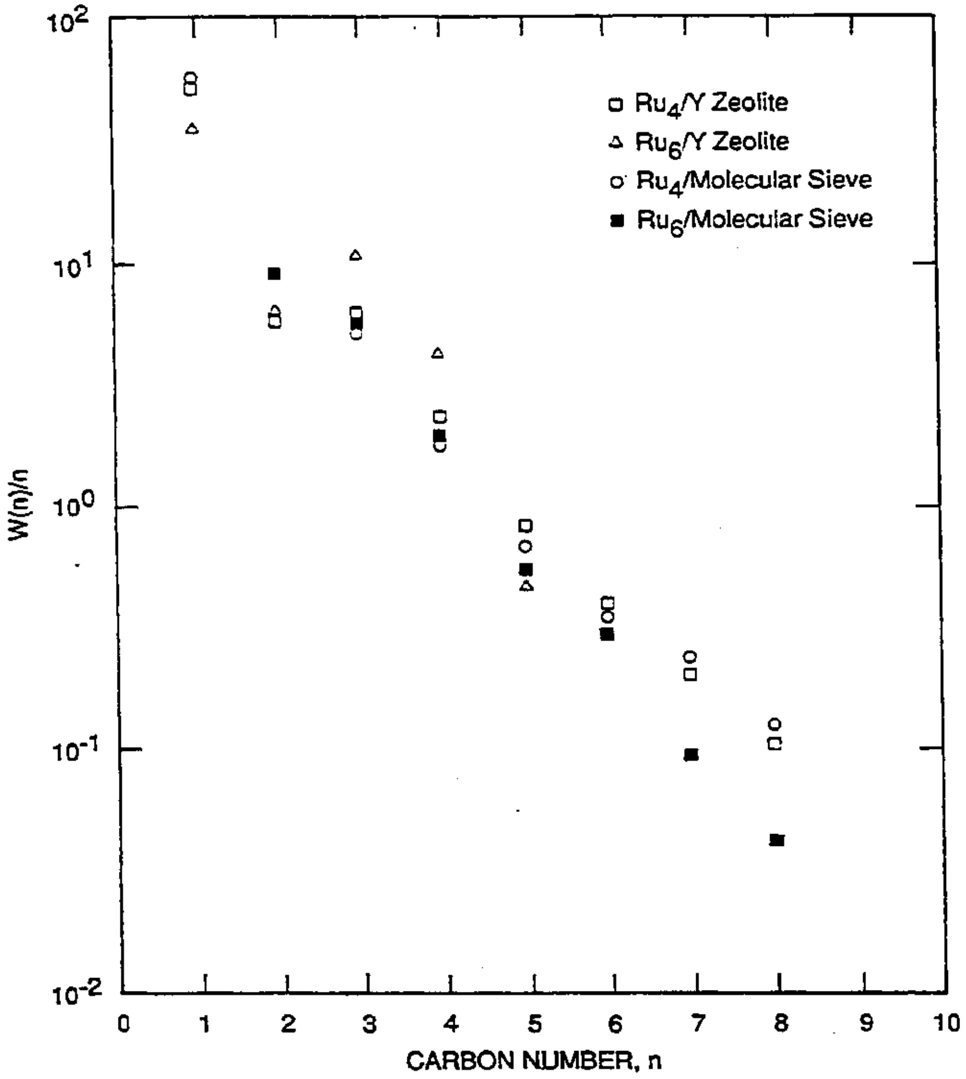

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FIGURE 1 SCHULZ-FLORY PLOT OF THE HYDROCARBON PRODUCT DISTRIBUTION FOR RUTHENIUM CLUSTER CATALYSTS AT 523 K, 100 kPa, AND $H_2/CO = 1.0$.

initial FTS and water gas shift (WGS) activities (Figure 2 and Table 2). Initially, the clean fused iron catalyst produced hydrocarbons with a chain growth probability factor of 0.43 (Figure 3) and a methane selectivity of 39% at 573 K. The methane selectivity changed to 63% as the catalyst deactivated after a 24-h run. (At 548 K, the clean catalyst had a chain growth probability of 0.48 with a 27% selectivity toward methane and showed no change with time). The activity of the clean fused iron catalyst could be restored temporarily to its original value by TPR in 1-atm hydrogen up to 773 K. This effect implicated carbon deposition as the cause for deactivation of the clean fused iron catalyst, as could be expected for low-H_2 synthesis gas.

Unlike the clean catalyst, which deactivated to one-third of its original activity with H_2:CO = 1:1 synthesis gas at 573 K, the 20% sulfur-treated catalyst maintained its activity throughout the 24-h synthesis run. The 20% sulfur-treated catalyst had a chain growth probability of 0.44 and a methane selectivity of 24% at both 548 K and 573 K. The activity of the sulfur-treated catalyst was about one-third the initial activity of the clean catalyst at 548 K but was similar to that of the clean catalyst at 573 K at steady state. Compared with the steady-state FTS performance of the clean catalyst, the 20% sulfur-treated fused iron catalyst demonstrated a twofold reduction in methane selectivity at 573 K (see Figure 2).

The series of sulfur-treated fused iron catalysts showed a minimum in methane selectivity (Figure 4) at roughly 50% saturation coverage. The olefin production rate showed little change from that of the clean catalyst, but the paraffin production rate (including methane) dropped significantly.

Precipitated Iron Catalysts--The clean and sulfur-treated K- and Cu-promoted precipitated iron catalysts prepared during the previous quarter were tested for FTS and found to be 68% and 48% selective toward methane at 573 K and steady-state reaction. It was difficult to prepare a sulfur-treated precipitated iron FTS catalyst at a desirable fractional

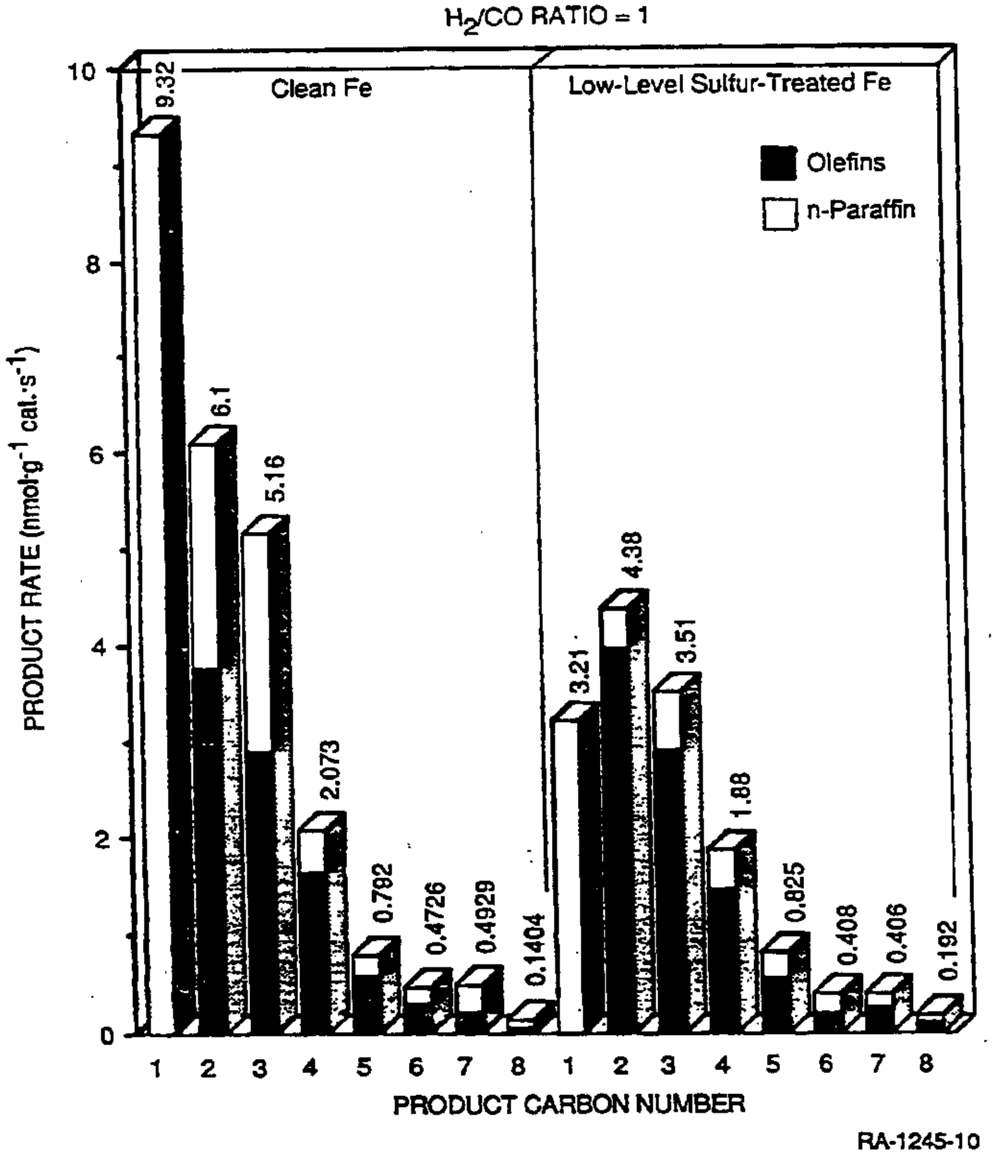

FIGURE 2 FISCHER-TROPSCH SYNTHESIS AT 573 K AND 100 kPa ON CLEAN AND LOW-LEVEL SULFUR-TREATED FUSED IRON CATALYSTS.

Table 2

FTS PERFORMANCE[a] OF CLEAN AND LOW-LEVEL SULFUR-TREATED IRON CATALYSTS

Catalyst	Temp	Run Duration	Product Rate[b] [nmol(g cat)$^{-1}$s^{-1}]												α[c]	β[d]	Methane[e] Selectivity
	(K)	(h)	CO_2	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	Total			
Fused Fe (clean)	548	23	33.53	5.03	2.49	1.44	0.63	0.28	0.15	0.115	0.052	0.015	0.0093	20.60	0.48	2.2	27
	573	2	75.50	9.32	3.05	1.72	0.62	0.22	0.11	0.092	0.022	0.0087	0.0064	25.78	0.43	1.4	39
		22	17.34	4.54	0.70	0.31	0.099	0.034	0.016	0.0043	---	---	---	7.56[f]	0.36	3.9[g]	63
Fused Fe (Sulfur Treated) $\theta_s = 0.2$)	548	22	15.74	1.56	0.995	0.54	0.22	0.077	0.036	0.025	0.014	0.0031	---	6.97[h]	0.43	11.7	25
	573	22	51.47	3.21	2.19	1.17	0.47	0.165	0.068	0.058	0.024	0.0027	0.0019	14.85	0.45	3.5	24

[a] Reaction conditions: H_2:CO = 1.0, P = 100 kPa, GHSV = 1170 h^{-1}.

[b] Includes n-paraffins and α-, β-olefins; total = total moles carbon converted into hydrocarbons.

[c] Mean chain growth probability factor.

[d] Average olefin to paraffin ratio for C_2-C_6 fraction, except where noted.

[e] C_1 rate/(total rate) x 100%.

[f] C_1-C_7 fraction.

[g] Average olefin to paraffin ratio for C_2-C_5 fraction.

[h] C_1-C_9 fraction.

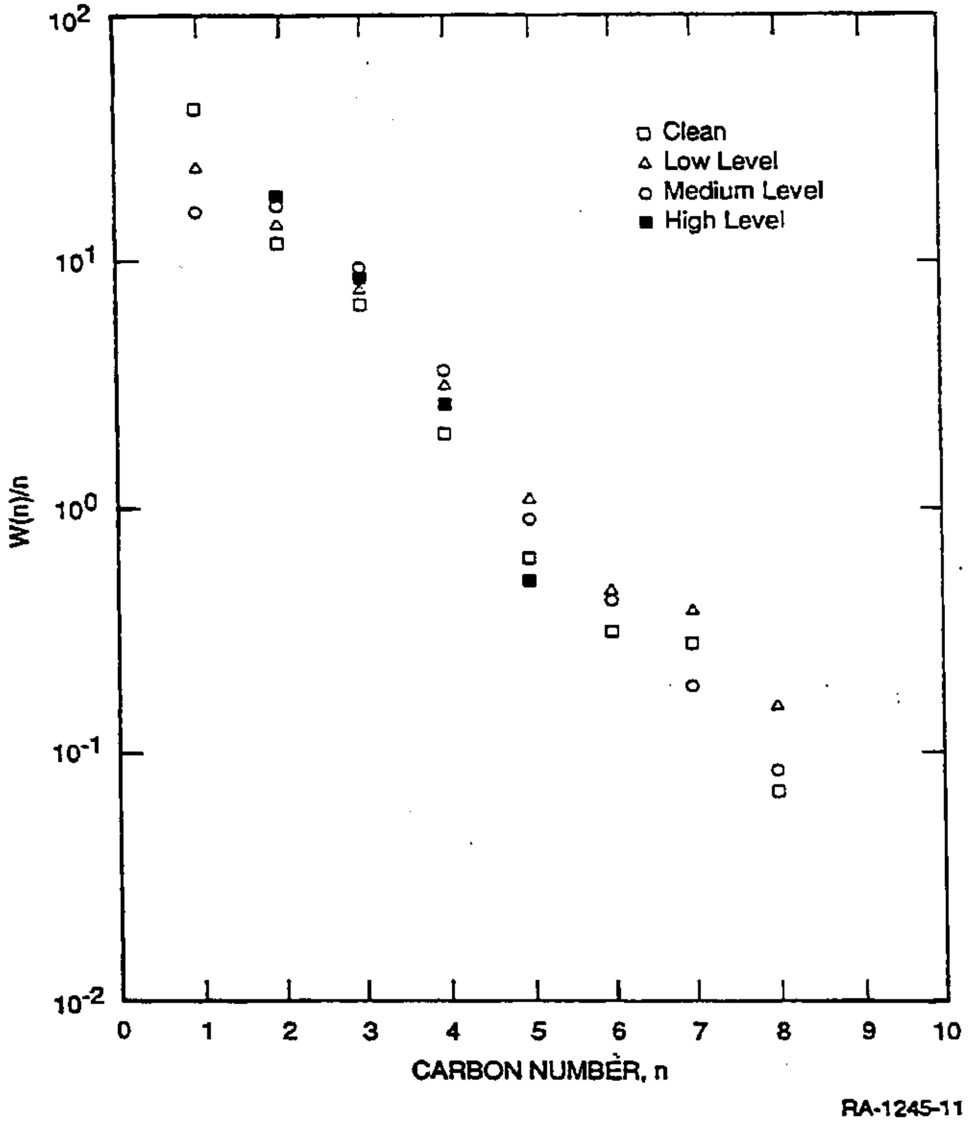

FIGURE 3 SCHULZ-FLORY PLOT OF THE HYDROCARBON PRODUCT DISTRIBUTION FOR CLEAN AND SULFUR-TREATED FUSED IRON CATALYSTS AT 573 K, 100 kPa, AND $H_2/CO = 1.0$.

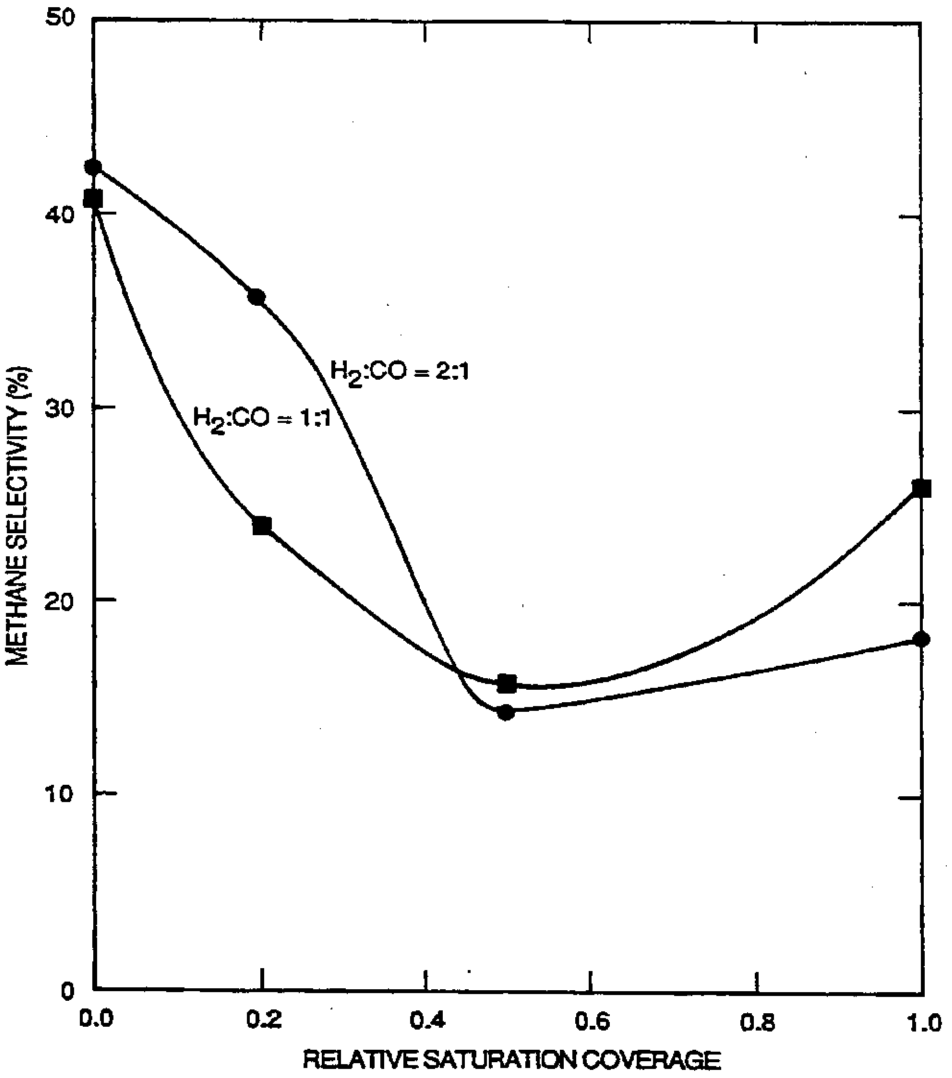

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FIGURE 4 FISCHER-TROPSCH SYNTHESIS AT 573 K, 100 kPa ON FUSED IRON CATALYSTS.

monolayer coverage because there is no reliable measure of true metal surface area of the potassium-promoted precipitated catalyst. Moreover, even at what appeared to be full-saturation sulfur coverage ($\Theta_s = 1.0$), the sulfur-treated precipitated iron catalyst remained more selective toward methane (48%) than the fused iron catalysts.

No further testing was done on the promoted precipitated iron catalyst because of its instability during sulfur treatment and its high selectivity for methane compared with that of the standard fused iron catalyst. The unpromoted alumina-supported cobalt catalyst should be easier to characterize without interference from the alkali promoter. With Co/Al_2O_3, the effect of sulfur treatment on the methane selectivity and olefin-to-paraffin ratio can be evaluated without ambiguity.

Analysis of Hot-Wax Trap Product--A hot-wax trap was installed at the exit of the FTS reactor. The trap was designed to collect C_{12+} hydrocarbons when operated at 393 K. The condensed wax was dissolved in toluene and analyzed by field ionization mass spectrometry (FIMS) to determine the distribution and chain growth probability factor of higher hydrocarbons. This supplemental analysis may prove important, especially for the ruthenium cluster catalysts on zeolite and molecular-sieve supports, because Ungar and Baird* have shown that, after appropriate activation, a cobalt supported on sodium-Y zeolite catalyst is shape selective for the hydrogenation of CO to alkenes with a cutoff at C_8.

FIMS provides a good supplemental analysis of the higher hydrocarbons in the FTS reaction. It should give an accurate quantitative measurement for molecules of the same class (e.g., alkanes, alkenes, aromatics), although sensitivity between classes can vary. The hot-wax trap was effective in collecting higher hydrocarbons, as evidenced by the FIMS analysis of FTS results for the clean and sulfur-treated fused iron catalysts (Figure 5). The clean fused iron catalyst

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*K. Ungar and M. C. Baird, J. Chem. Soc., Chem. Commun. 643-645 (1986).

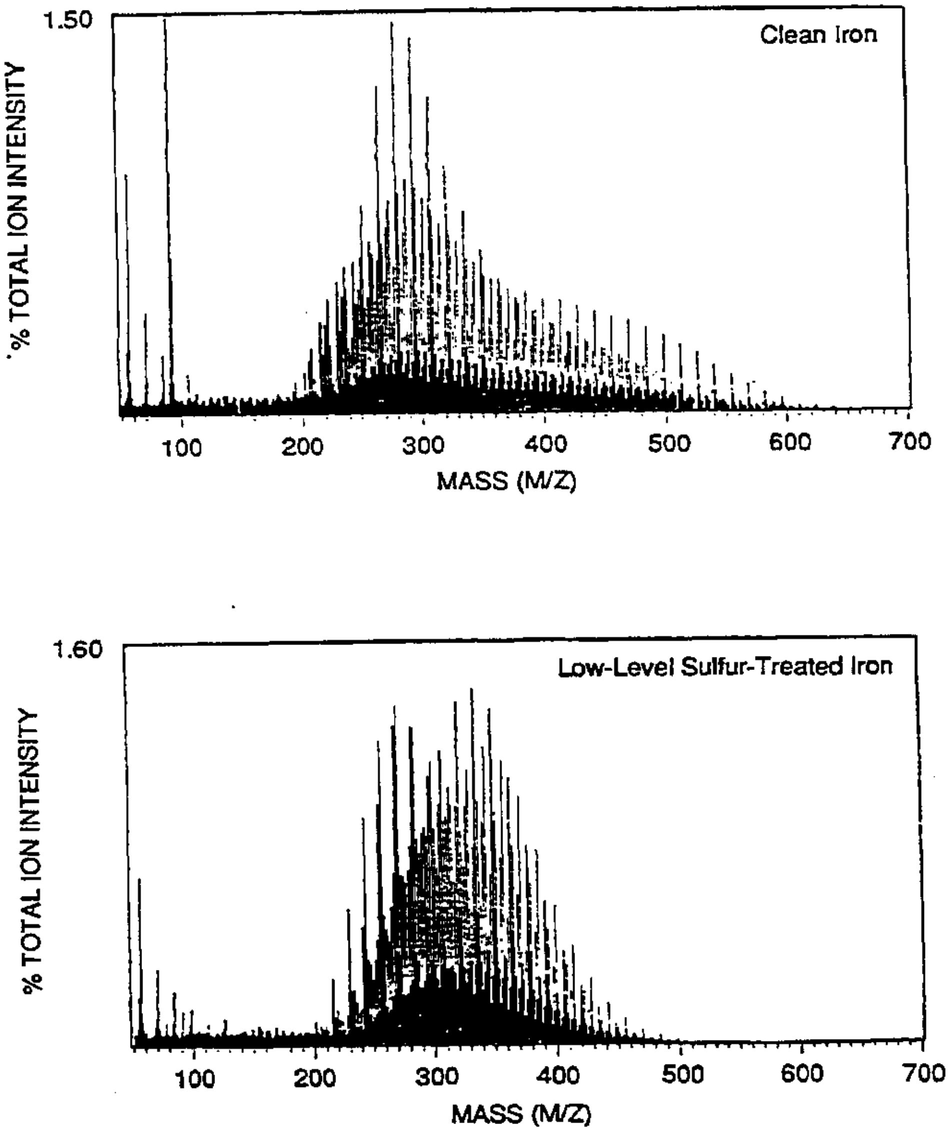

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FIGURE 5 FIMS ANALYSIS OF HOT WAX FOR CLEAN AND LOW-LEVEL SULFUR-TREATED FUSED IRON FT CATALYSTS.

had hydrocarbon product up to C_{45}, whereas the sulfur-treated fused iron catalyst had observable hydrocarbon product only up to C_{35} with a lower chain growth probability factor.

The trap was operated under identical conditions during FTS testing of the ruthenium cluster catalysts, and all sampling lines were heated to 30°C higher than the hot-wax trap. However, wax collected in the trap only for the Ru_4 cluster supported on sodium-Y Zeolite. The ruthenium cluster catalysts (except Ru_6 on sodium-zeolite, which had much lower activity) had FTS activities and chain growth probability factors similar to those of the fused iron catalysts. Yet the cluster catalysts produced negligible hot-wax product, suggesting that either the ruthenium cluster catalysts have a sharp drop in hydrocarbon production rate beyond C_{12} or the zeolite support adsorbed the higher-molecular-weight products.

TECHNICAL STATUS

The following work has been performed during the past quarter:

- Characterized and tested the series of supported Ru, Ru_4, and Ru_6 cluster catalysts for FTS activity and selectivity.
- Prepared, characterized, and tested low-level sulfur-treated fused iron catalysts for FTS activity and selectivity.

During the next quarterly period (April–June 1987), we expect to perform the following tasks:

- S/Co—Prepare, characterize, and test high-level and low-level sulfur-treated alumina-supported cobalt catalysts for FTS activity and selectivity.
- Ru monomers—characterize and test monoruthenium cluster catalysts supported on alumina, sodium Y-zeolite, and molecular sieve for FTS activity and selectivity.
- Initiate Task 4—initiate Task 4 using the most promising catalysts, those with high FTS activity and low selectivity for methane.