



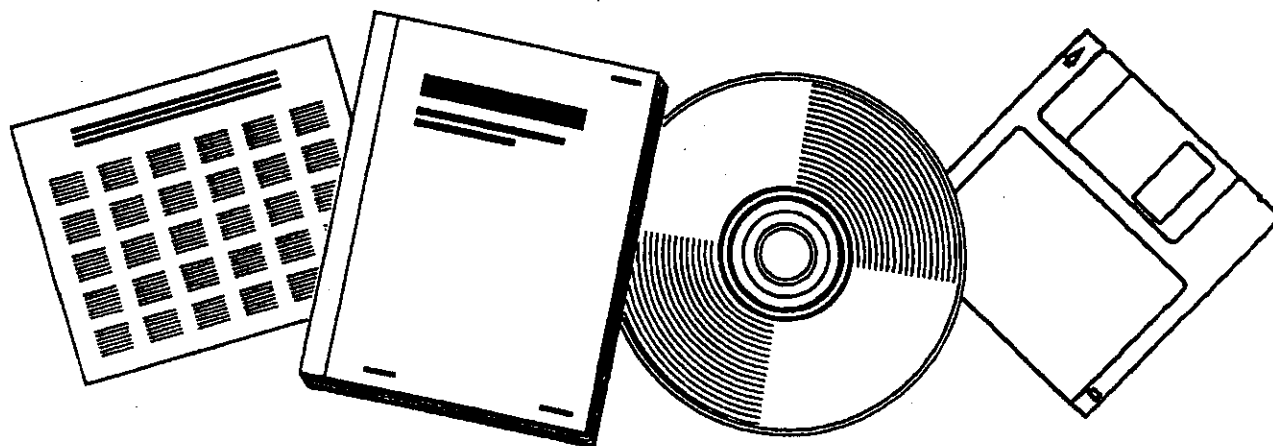
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**IMPROVED FISCHER-TROPSCH SYNTHESIS
CATALYSTS FOR INDIRECT COAL LIQUEFACTION:
QUARTERLY TECHNICAL PROGRESS REPORT NO. 7,
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IMPROVED FISCHER-TROPSCH SYNTHESIS CATALYSTS FOR INDIRECT COAL LIQUEFACTION

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SUMMARY

Three monomeric supported ruthenium catalysts were evaluated for Fischer-Tropsch performance with 1:1 H₂:CO synthesis gas at 1 atm. This effort completes the FTS evaluation of a series of nine supported multiatomic and atomic ruthenium catalysts prepared via organometallic reactions of tetra- and hexaruthenium hydridocarbonyls and allyl monoruthenium carbonyl complexes with acid sites on three support materials, alumina, sodium Y zeolite, and molecular sieve. The product distribution of the three monomer catalysts was remarkably dependent on the nature of the support. The ruthenium catalyst supported on sodium Y zeolite had superior FTS performance relative to a conventionally prepared alumina-supported ruthenium catalyst during a 24-h run at 523 K with 1:1 H₂:CO synthesis gas at 1 atm. Its chain growth factor was higher (0.57 vs 0.47), methane selectivity lower (45 wt% vs 58 wt%), and olefin-to-paraffin ratio for light hydrocarbons higher (2.2 vs 1.3). The FTS results for the molecular sieve catalyst under the same reaction conditions were inferior with low chain growth parameter (0.23) and high methane selectivity (77 wt%). The C₂₊ hydrocarbon synthesis rates of all the ruthenium catalysts were comparable.

The effect of high-level sulfur chemisorption on the FTS performance of alumina-supported cobalt was also examined. The cobalt FTS catalyst was prepared by impregnation of a moderate surface area (80 m²g⁻¹) alumina support with cobalt nitrate to 10 wt% reduced cobalt. The dispersion of the cobalt was 0.03 based on H₂ and CO chemisorption and titration with H₂S chemisorption. The untreated cobalt catalyst had, as expected, higher activity and higher methane selectivity relative to the standard fused iron catalyst. After uniform sulfur chemisorption to approximately 90% saturation coverage, the steady-state (20 h) activity of the cobalt catalyst with 1:1 H₂:CO synthesis gas at 523 K and 1 atm decreased an order of magnitude with only modest decreases in methane selectivity (32 wt% vs 45 wt%) and chain growth parameter (0.48 vs 0.58).

Work on Task 4, the investigation of selected catalysts for FTS under higher pressure, is under way with modification of an autoclave for use as a slurry reactor at 1000 psi and modification of the FTS testing system for fixed-bed operation at 300 psi. Preparation and examination of a cobalt catalyst with approximately 50% sulfur coverage is planned for next quarter as the final sulfur treatment task.

EXPERIMENTAL RESULTS

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

Surface-confined Fischer-Tropsch synthesis (FTS) catalysts were synthesized in Task 1, using a pendant hydrocarbyl functional group that reacts with hydroxyl groups on the surfaces of several support materials. This work consisted of 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.

These subtasks and the progress to date are described below.

Tasks 1A and 1B--We previously 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 the facile reaction in THF at 25°C of the Al-Ru₄ and Al-Ru₆ complexes with Bronsted acid sites on alpha-alumina (Kaiser), a sodium Y-zeolite (Union Carbide LZ-Y52), and a molecular-sieve zeolite (Union Carbide 5A). 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.

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 α-alumina.

Elemental analyses of the monomeric Ru catalysts on all the supports were performed by a commercial analytical laboratory (Galbraith Laboratory). The results (Table 1) showed the ruthenium loadings ranged from 0.31 wt% for Ru/Na Y-zeolite to 0.37 wt% for Ru/α-alumina.

Task 2: Sulfur Treatment of Fisher-Tropsch Catalysts

An unpromoted cobalt catalyst was prepared from an aqueous solution of cobalt(II)nitrate [Co(NO₃)₂·6H₂O, Alfa Products, puratronic grade] by the method of incipient wetness on Harshaw AL-0104 alumina with 88 m²g⁻¹ BET surface area and crushed and screened to 0.3-0.5 mm mean diameter. The catalyst was then dried in air at 400 K for 24 hours. The final weight ratio was Co:Al₂O₃ = 1:10.

A fully sulfided (100% monolayer sulfur cover) cobalt catalyst was prepared for titration of the total active metal surface area by sulfur chemisorption and as a high-level sulfur-treated cobalt catalyst to be tested for Fischer-Tropsch synthesis activity and selectivity. Excess

Table 1
 FTS PERFORMANCE^a OF RUTHENIUM MONOMER AND CONVENTIONAL RUTHENIUM CATALYSTS

Catalyst	Ru Loading (wt%)	Run Duration (h)	Product Rate ^b (mmol g _{cat} ⁻¹ h ⁻¹)										Methane ^e Selectivity			
			CO ₂	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉		Total	α ^c	β ^d
Ru/Zeolite (Na-Y Zeolite)	0.31	24	2.31	3.54	0.47	0.55	0.22	0.077	0.075	0.048	0.076	-	8.39 ^f	0.57	2.2	45
Ru/5 Å Molec. Sieve	0.37	24	3.16	12.19	0.81	0.57	0.155	0.079	-	-	-	-	16.298	0.23	1.4	71
Ru/Al ₂ O ₃	0.15	24	1.09	2.82	0.51	0.594	0.198	0.058	0.022	0.007	0.005	-	6.97 ^f	0.37	3.2	44
Conventional Ru/Al ₂ O ₃	0.5	24	2.1	6.32	0.65	0.684	0.23	0.081	0.040	0.019	0.008	0.004	11.51	0.47	1.3	58

^aReaction conditions: H₂/CO = 1.0, P = 100 kPa, T = 523 K, GHSV = 600 h⁻¹.

^bIncludes n-paraffins and α-, β-olefins; total = total carbon converted into hydrocarbons. The rates are expressed as mmol hydrocarbon produced per second per gram of catalyst (including the support).

^cMean chain growth probability factor for the C₃₊ fraction.

^dAverage olefin-to-paraffin ratio for the C₂-C₃ fraction.

^eCH₄ rate/(total rate on a carbon atom basis) x 100%.

^fC₁-C₆ fraction.

^gC₁-C₃ fraction.

H₂S was injected into the sulfur chemisorption gas recirculation system containing freshly reduced catalyst at 773 K, the amount of sulfur chemisorbed corresponding to a metal surface area of 22.5 m²g⁻¹. The catalyst was equilibrated overnight at 773 K, and the gas-phase H₂S concentration was measured over a range of temperatures and the isostere was plotted in Figure 1. A comparison of the current results with previously published isosteres for cobalt powder¹ indicates that the sulfur coverage approached saturation. Further evidence of the high sulfur coverage was the greatly reduced H₂ and CO adsorption capacities, as discussed below.

Task 3: Characterization and Testing of the FTS Catalysts

Activation of Ruthenium Monomer Catalysts--The monoruthenium catalysts supported on LZY-52 (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. Propene 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.

After the FTS reaction, the ruthenium cluster catalysts were unloaded from the reactor without exposure to air and stored under dry N₂. Samples were sent to a commercial laboratory for elemental analysis to check for loss of ruthenium through volatilization of ruthenium carbonyls.

FTS Testing of the Ru Monomer Catalysts--The Fischer-Tropsch synthesis reaction was conducted with 1-atm synthesis gas of fixed composition (H₂:CO = 1:1) at 523 K for the monoruthenium cluster catalysts on various supports and conventional 0.5 wt% ruthenium on alumina. Gas hourly space velocities (GHSV) between 600 h⁻¹ and 1200 h⁻¹ were used to achieve differential conditions, depending on the catalysts

¹J. G. McCarty and H. Wise, J. Chem. Phys. 76, 1162 (1982).

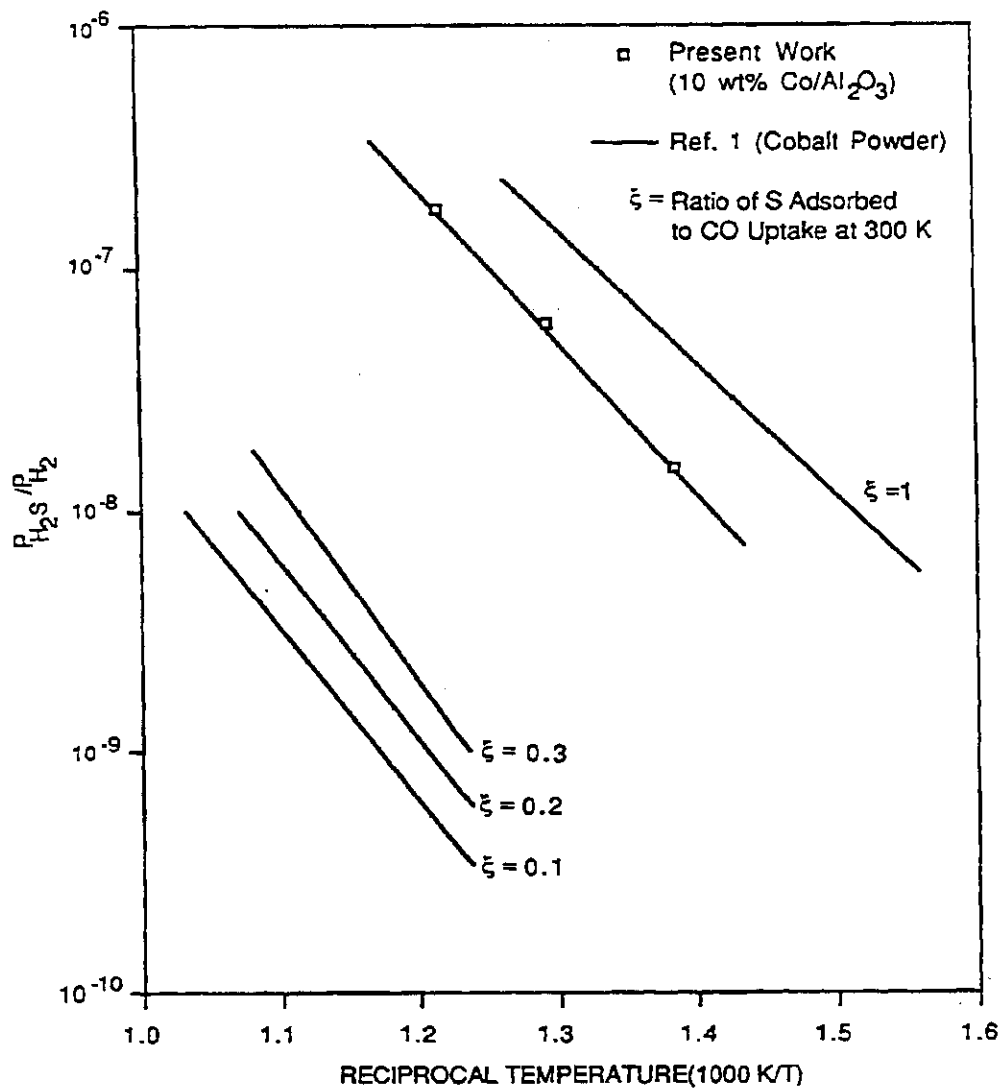


FIGURE 1 SULFUR CHEMISORPTION ISOTHERES ON COBALT/ Al_2O_3 AND COBALT POWDER

activity. All the FTS experiments were conducted under differential conditions with a maximum CO conversion of 5%.

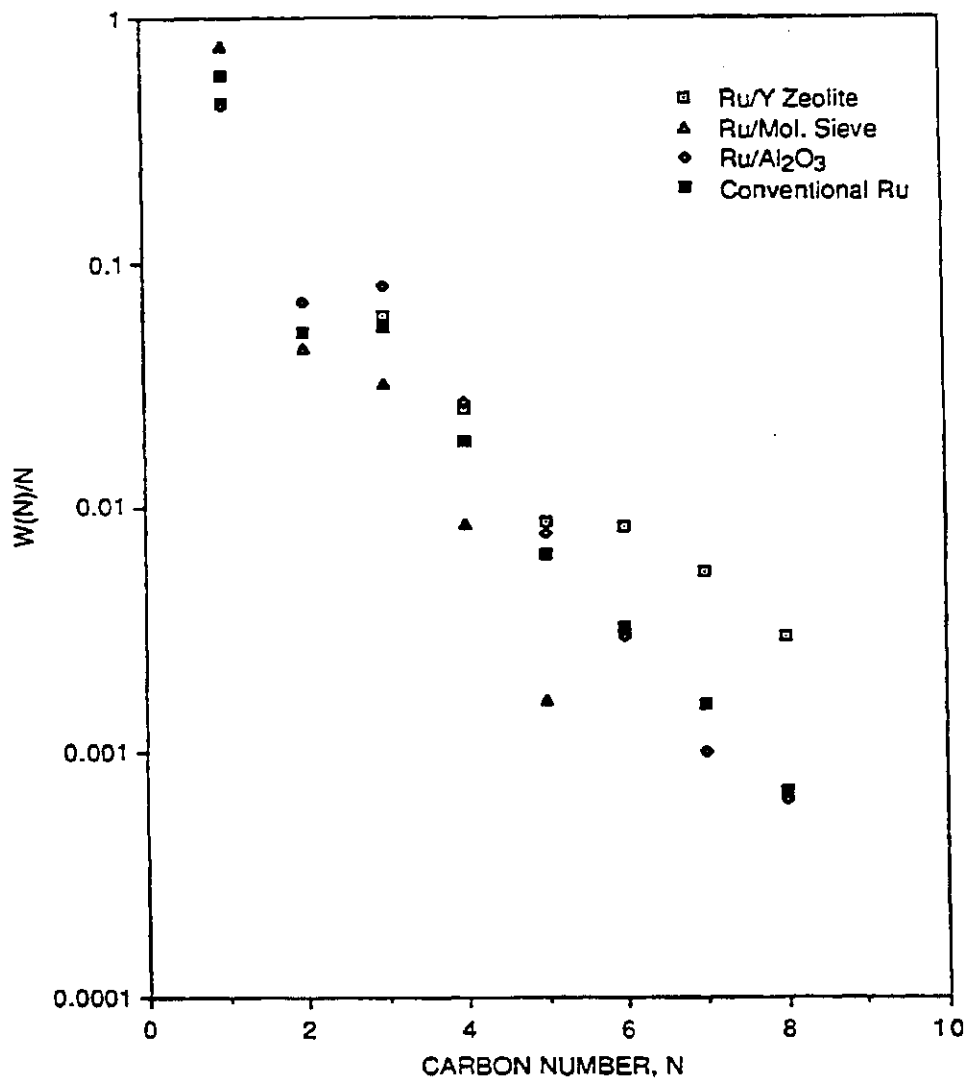
Of the three monoruthenium cluster catalysts tested, the one supported on molecular sieve had the highest FTS activity but with a high 77% selectivity toward methane (Table 1). The conventional 0.5 wt% ruthenium was also tested for comparison with the ruthenium cluster catalysts. It had a 58% selectivity toward methane and a chain growth probability of 0.48. Both the monomers supported on sodium Y zeolite and alumina had activities comparable to the conventional ruthenium catalyst, had an average methane selectivity of 45%, and their chain growth probabilities were 0.57 and 0.38, respectively (see Figure 2 and Table 1).

Characterization of the Cobalt Catalyst by CO and H₂ Chemisorption--

After reduction in hydrogen for 4 h at 773 K, the specific surface area of the cobalt catalyst was determined by dynamic CO adsorption at 300 K. Known aliquots of gas containing 5.25% carbon monoxide in helium were passed through the reactor containing the catalyst until no further adsorption was observed. The fraction of CO adsorbed from each dose was determined from the difference between the integrated pulse area of the reactor doses and doses with the reactor bypassed. The active metal surface area of the catalyst (Table 2) was calculated from the amount of CO adsorbed per unit initial catalyst weight, assuming 1×10^{19} CO molecules adsorbed per square meter of reduced metal surface. After the surface area measurement, the catalyst was temperature-programmed in a stream of hydrogen at 0.167 K s^{-1} up to 623 K to remove any carbon monoxide adsorbed on the catalyst.

Hydrogen chemisorption was performed using a static BET surface area measurement apparatus. Aliquots of 99.99% pure H₂ were injected into a calibrated volume, which was then expanded into the evacuated sample cell containing the reduced catalyst sample. The metal surface area (Table 2) was then calculated from the total amount of hydrogen adsorbed.

Surface area measurements were performed on the clean and fully sulfided cobalt catalysts. As expected, little CO adsorption and no H₂ adsorption were observed for the high-level sulfur-treated catalyst.



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FIGURE 2 SCHULZ-FLORY-ANDERSON PLOT OF THE HYDROCARBON PRODUCT DISTRIBUTION FOR RUTHENIUM CLUSTER AND CONVENTIONAL RUTHENIUM CATALYSTS AT 523 K, 100 kPa, AND H₂/CO = 1.0

Table 2

EFFECT OF SULFUR TREATMENT ON H₂ AND CO ADSORPTION CAPACITIES
AND METHANE SELECTIVITY DURING FTS^a OF 10 wt% Co/Al₂O₃

Sulfur Coverage, θ_s^b	Total H ₂ Uptake ($\mu\text{mol g}^{-1}$)	Total CO Uptake ($\mu\text{mol g}^{-1}$)	Methane Selectivity ^c (wt%)
0	97	189	45
0.9	0	4.3	30

^aH₂:CO = 1:1, T = 523 K, GHSV = 4680 h⁻¹, P = 100 kPa, 24-h run.

^b θ_s - Ratio of S adsorbed to CO uptake at 300 K.

^cCH₄ rate/(total rate) x 100%.

FTS Testing of Cobalt Catalysts--The clean cobalt catalyst had higher FTS activity than the fused iron catalysts (Table 3). Initially, the FTS clean cobalt catalyst was 30 times higher than the fused iron catalyst at 548 K and 10 times higher after a 24-h synthesis run. The clean cobalt catalyst produced hydrocarbons with a chain growth probability factor of 0.47 and a methane selectivity of 43% at 548 K. The chain growth probability factor increased slightly to 0.54 (see Figure 3), but the methane selectivity remained unchanged as the catalyst deactivated after a 24-h run. At 523 K, the clean catalyst had a chain growth probability of 0.58 with 45% selectivity toward methane and showed no change with time. The activity of the cobalt catalyst could be restored temporarily to its original value by TPR in 1-atm hydrogen up to 773 K. Therefore, carbon deposition was the probable cause of deactivation of the clean cobalt catalyst, as expected from use of the low- H_2 synthesis gas.

The hydrocarbon product distribution of the clean fused iron and clean cobalt catalyst at 573 K and 548 K, respectively, were similar (Figure 4). The cobalt catalyst possesses a higher olefin-to-paraffin selectivity (alkene/alkane ratio = 10) for light hydrocarbons and a ten-fold higher FTS activity at lower temperature than the clean fused iron catalyst.

Task 4: Evaluation of Improved FTS Catalysts

The objective of Task 4 is to accurately determine properties such as the activity, product distribution (with emphasis on light and heavy hydrocarbons), wax accumulation, and deactivation tendency of selected improved catalysts compared with those of the standard fused iron catalysts reactor conditions. Modification of the fixed-bed FTS testing system for operation at 1.5 to 2 MPa is under way. The fixed-bed reactor system will be used to determine FTS reaction kinetics for the sulfur-treated fused iron and perhaps cobalt catalysts at 548 K to 598 K, with emphasis on methane selectivity and alkene/alkane ratio of light hydrocarbons.

Table 3
 FTS PERFORMANCE^a OF CLEAN AND HIGH-LEVEL SULFUR-TREATED COBALT CATALYSTS

Catalysts	Temp (K)	Run Duration (h)	Product Rate ^b (nmol g _{cat} ⁻¹ h ⁻¹)										Methane ^c Selectivity				
			CO ₂	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉		C ₁₀	Total	α ^c	β ^d
10 wt% Co on Al ₂ O ₃ (clean)	523	20	33.79	113.46	9.66	14.67	8.94	4.56	2.81	1.54	0.895	0.51	0.337	278.1	0.58	3.6	41
	548	2	78.75	261.97	24.41	39.86	18.95	7.32	3.55	1.62	0.747	0.349	0.223	586.8	0.47	4.2	45
		24	29.99	86.67	15.17	12.82	6.47	2.91	1.76	0.93	0.524	0.263	0.159	221.0	0.54	10.6	39
10 wt% Co on Al ₂ O ₃ (high level sulfur)	523	21	2.75	2.86	1.02	0.69	0.28	0.14	0.08	0.06	-	-	-	9.69	0.49	-	30

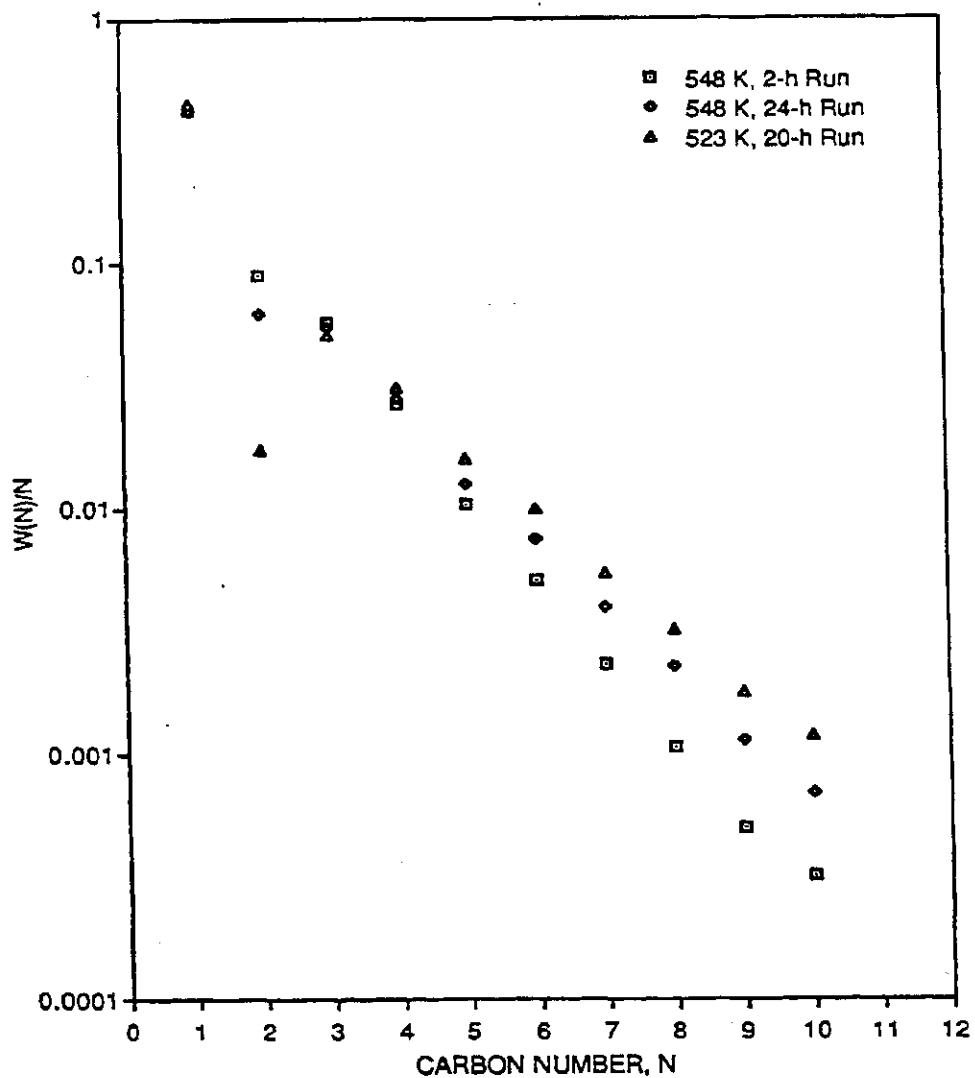
^aReaction Conditions: H₂/CO = 1.0, P = 100 kPa, GHSV = 1170 h⁻¹.

^bIncludes n-paraffins and α- and β-olefins; total = carbon converted into hydrocarbons.

^cMean chain growth probability factor for C₁ hydrocarbons.

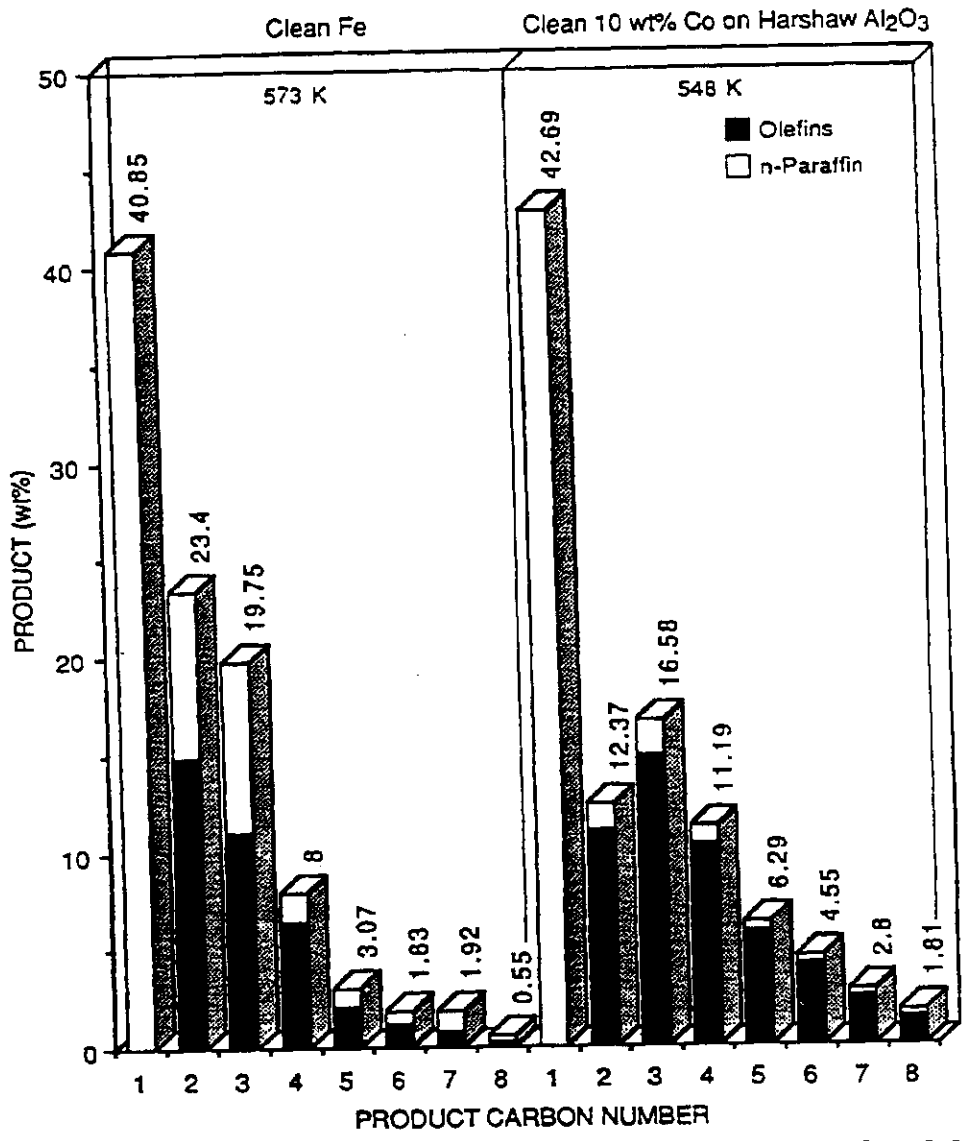
^dAverage olefin-to-paraffin ratio for C₂-C₆ fraction.

^eCH₄ rate/(total rate) x 100%.



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FIGURE 3 SCHULZ-FLORY-ANDERSON PLOT OF THE HYDROCARBON PRODUCT DISTRIBUTION FOR COBALT ON ALUMINA CATALYST AT 100 kPa AND $H_2/CO = 1.0$



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FIGURE 4 FISCHER-TROPSCH SYNTHESIS AT 100 kPa AND H₂/CO RATIO = 1.0 ON CLEAN FUSED IRON AND CLEAN COBALT CATALYSTS AT 573 K AND 548 K, RESPECTIVELY

Three promising improved catalysts, the medium level sulfur-treated fused iron, the tetra-ruthenium cluster support on sodium-Y zeolite catalysts, and mono-ruthenium on 5A molecular sieves will be tested in a slurry reactor. These catalysts will be compared to the standard fused iron and conventional alumina-supported ruthenium catalysts. The medium level sulfur-treated fused iron was chosen because of its decreased methane and increased olefin yields. The two organometallics were chosen for further study because they show reduced heavy hydrocarbon yield by our GC analysis while maintaining relatively good overall activity.

A 300-mL stirred autoclave is being modified for FTS testing. The stirred autoclave, operating at 473 K to 523 K and 1.5 to 2 MPa, will be used to determine the hydrocarbon product distribution of the improved catalysts and the standard fused iron catalyst up to approximately C₄₀ hydrocarbons. Field ionization mass spectroscopy (FIMS) will be used for wax analysis, with pure wax compounds and wax samples from Professor Satterfield's experiments at MIT serving as calibration and reference standards.