FE-2467-1
Distribution Category UC-90d

TRANSITION METAL-GRAPHITE CATALYSTS FOR PRODUCTION OF LIGHT HYDROCARBONS FROM SYNTHESIS GAS

Quarterly Report for the Period
August 1, 1976 - October 31, 1976

Michael P. Rosynek

Texas A & M University
Department of Chemistry
College Station, Texas 77843

Date Submitted - November 1976

PREPARED FOR
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

Under Contract No. E(49-18)-2467

ep

ABSTRACT

Suitable methods have been established for the preparation of alkali and transition metal-graphite catalysts. These involve thermal treatment in vacuo at 300-400°C of appropriate graphite-transition metal chloride mixtures to effect intercalation of the metal chloride, followed by reduction with alkali metal in vacuo at 250-300°C, and subsequent removal of excess alkali metal by distillation.

Preliminary catalytic testing of sodium and potassium graphites for the Fischer-Tropsch synthesis at 300°C and at atmospheric pressure reveals behavior quite unlike that exhibited by conventional supported transition metal catalysts. Notable differences include a complete absence of carbon dioxide from the reaction product in all cases, and, in the case of potassium graphite, exclusive confinement of product distribution to C_1-C_3 paraffins. In addition, a considerable fraction of the carbon monoxide reactant that is admitted to a fresh catalyst sample becomes irreversibly adsorbed in an unreactive form that may inhibit the overall reaction rate.

I. OBJECTIVE AND SCOPE OF WORK

The objective of this research is the development of a novel process for the production of petrochemical feedstocks based on coal or other carbonaceous materials. Specifically, the project is to investigate the catalytic activity and selectivity of novel alkali and transition metal-graphites in producing light (C_1-C_3) hydrocarbons from H_2/CO synthesis gas via the Fischer-Tropsch process.

II. SUMMARY OF PROGRESS TO DATE

A comparison of actual research progress to date vs. project schedule is summarized in the "Project Plan and Progress Chart" shown in Fig. 1. Because catalytic behavior of the resulting metal-graphites is ultimately the most important criterion to be applied in establishing optimum procedures for catalyst preparation (Tasks 1a and 1b), comparative testing of prepared catalysts for Fischer-Tropsch activity under atmospheric pressure conditions (Tasks 2a and 2b) was initiated during the current reporting period, even though the latter Tasks were not originally scheduled to begin until the second quarter. Technical details of research progress during the first contract quarter are contained in the following Section.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Work during the initial contract reporting period has been performed in three principal areas: 1) acquisition and assembly of instruments and equipment, and subsequent construction of experimental systems to be used for catalyst preparation and testing; 2) exploration and evaluation of suitable preparation methods for graphite-based catalysts, and establishment of optimum preparation techniques (Tasks 1a and 1b), and 3) preliminary comparative testing of a commercial supported iron catalyst and of sodium and potassium graphites for catalytic activity and selectivity in the Fischer-Tropsch synthesis (Tasks 2a and 2b). As noted in the previous Section, investigations in areas (2) and (3) have been largely simultaneous, but will be discussed separately for purposes of clarity. Details of progress in each of the three areas are described in the following Sub-Sections

A. Systems Construction

1. Catalyst Preparation and Handling Chamber

A controlled-atmosphere chamber has been assembled to enable handling of anhydrous transition metal chlorides and pure alkali metals, required for catalyst preparations, in an oxygen- and water-free environment. The system is based on a Kewaunee Co. model 2C-610 vacuum dry box, having a total internal volume of 70 liters, and is equipped with a Sargent-Welch model 8815 direct-drive rotary vacuum pump (150 liters/min) operated through a refrigerated cold trap. A Torsion Co. model DWM-2 balance having a sensitivity of 2 mg is permanently contained within the chamber and allows in situ weighing of all catalyst components during the preparation procedure. Pressure measurements are made with a Wallace and Tiernan Co. model 61-050 aneroid gauge (0-800 torr) and a Fredericks Co. model 2C thermocouple gauge (0-1000 microns). Purified nitrogen is supplied to the chamber through a Linde 5A molecular sieve drying train and liquid nitrogen-cooled trap. The vacuum/pressure gauges and cold traps, plus associated valves, by-passes, and all-metal manifolding have been mounted on a vertical panel attached directly to the chamber, thus making the entire system self-contained.

In operation, required reagents and materials are placed within the box; the glove ports are evacuated initially and then isolated, and the main chamber is evacuated to < 100 microns. The box is then quickly filled with purified nitrogen to atmospheric pressure, and the evacuation/re-filling procedure is repeated. The entire systen is fully operational and has been used to maintain working O_2/H_2O levels of < 20 ppm for 2-3 hours, which is judged adequate performance for the intended studies.

2. Atmospheric Pressure Catalytic Testing System

An all-glass reaction system has been constructed to enable testing of prepared catalysts for activity and selectivity behavior in Fischer-Tropsch syntheses. The system is of the recirculation (stirred-batch) type, having a total volume of 350 ml, and consists of a mixing vessel (which contains ~ 85% of the system volume), an isolatable by-pass trap, a U-shaped reactor with spiral pre-heater section, and a circulation pump consisting of appropriate check valves and a glass-enclosed iron piston activated by a pulsed toroid. Additional provisions exist for introducing hydrogen and carbon monoxide reactants into the system through refrigerated traps. The reactor containing the catalyst bed is thermostatted to ± 1°C of the desired reaction temperature in a Hoskins Co. model FA-120 crucible furnace energized by a Thermolyne Co. model CP-12915 temperature controller. Reactor temperature is monitored by a Thermo-Electric Co. model 31606-011 digital readout connected to an iron-constantan thermocouple positioned in the furnace at the midpoint of the catalyst sample.

The reaction system is connected via greased stopcocks to appropriate pressure-measureing devices and to a conventional diffusion-pumped high vacuum gas handling system. Evacuation is achieved in two stages with a Lammert Co. model 10202 direct-drive rotary pump (42 liters/min) and a Varian model M-2 oil diffusion pump (175 liters/sec). Pressures are measured in three overlapping ranges with a calibrated Granville-Phillips Co. model 260 ionization/thermocouple gauge controller and a Validyne Co. model DM56A-895 variable capacitance manometer with digital readout to ± 0.1 torr and an accuracy of ± 0.2% of reading.

Analyses of reactant/product mixtures are accomplished by periodically expanding samples (0.3 vol %) from the circulating gas stream into a previously-evacuated sample loop of a gas sampling valve that is installed in a Carle Co. model AGC-111 gas chromatograph. Separation of gas mixtures containing hydrogen, carbon monoxide, carbon dioxide, water, methane, ethylene, ethane, propylene, propane, and C_4^+ materials has been successfully effected using a 1/8" x 12' stainless steel column packed with 80/100 mesh Porapak R and maintained at an isothermal oven temperature of 80°C. An entire analysis, including column backflush to elute C_4^+ components, requires less than 15 minutes. Output from the thermal conductivity detector of the gas chromatograph is displayed on a Linear Instruments Corp. model 252A/E1 strip-chart recorder equipped with an electronic integrator. Quantitative analyses of reaction product mixtures are based on integrated component peak areas, following appropriate corrections for differing thermal response factors.

3. Other Equipment

All of the equipment and experimental systems described in Sub-Sections A.1. and A.2. are intended solely for this project. Additional instruments and equipment available within our laboratory for this research, but not devoted to it, include a fully-equipped thermogravimetric analysis and gas adsorption apparatus, based on a Cahn Co. model RG recording electrobalance, for adsorption and surface area measurements of prepared catalysts and graphite substrates, and an Electronic Associates, Inc. model 1200 quadrupole residual gas analyzer for supplementary analyses of reaction product mixtures.

All acquisition, construction, and testing of instruments and equipment required for completion of Phase I of the project have been completed.

B. Evaluation of Catalyst Preparation Methods (Tasks 1a and 1b)

Our exploratory investigation of suitable catalyst preparation methods has been largely based on the previously-published work of Croft (J. Austral. Chem. Soc. 9, 184 (1956)) and Tamaru (U.S. Patent No. 3,842,121 (1974)), whose techniques appear to be generally applicable to the present research. Group VIB (Cr, Mo, W) and VIII (Fe, Co, Ni, Ru, Pd, Os, Pt) transition metals are intercalated into the graphite structure by weighing, in a moisture-free environment, appropriate amounts of the anhydrous metal chloride and powdered, ash-free, graphite (initial surface area, 20 m^2/g) into a tubular glass vessel. The mixture is evacuated at 25°C to $< 10^{-3}$ torr, isolated, and then heated in a static vacuum at 300-400°C for 3-6 hours, the optimum heating temperature varying only slightly with the identity of the metal chloride. For $FeCl_3$-graphite, for example, which is the first combination that we have begun to investigate, heating for 6 hours at 300°C provides satisfactory results. Intercalation of the less volatile $CrCl_3$, on the other hand, requires temperatures nearer 400°C and somewhat longer heating times. Maximum attainable intercalation levels, however, differ considerably for the various transition metal chlorides of interest, as shown by the results of Croft (and verified by us for $FeCl_3$), who used an excess amount of metal chloride in each case:

Metal Chloride	Maximum Intercalation Level (wt %)	Equivalent Molecular Formula
$CrCl_3$	76	C_4CrCl_3
$MoCl_5$	25	$C_{68}MoCl_5$
WCl_6	26	$C_{94}WCl_6$
$FeCl_3$	56	$C_{11}FeCl_3$
$CoCl_3$	55	$C_{11}CoCl_3$
$NiCl_2$	--	---
$RuCl_3$	3	$C_{556}RuCl_3$
$PdCl_4$	54	$C_{393}PdCl_4$
$OsCl_4$	--	---
$PtCl_4$	37	$C_{98}PtCl_4$

Materials containing less than the maximum attainable levels are easily obtained by adjusting the graphite/metal chloride ratio in the original mixture. In these cases, little non-intercalated metal chloride remains after heating, and washing is usually unnecessary.

Reduction of intercalated transition metal chlorides to the corresponding free metals is accomplished by adding a weighed excess (1:1 by weight of graphite) of alkali metal (sodium, potassium, rubidium, or cesium) to the reaction vessel under an oxygen- and moisture-free atmosphere, evacuating at 25°C to $< 10^{-3}$ torr, and then heating at 250-300°C for 3-4 hours. Excess alkali metal, required to ensure complete and intimate contact with the transition metal-graphite, is then removed by heating the vessel for an additional 6 hours under dynamic vacuum conditions. This procedure causes the alkali metal to distill out of the hot reaction tube and condense on its cooler walls above the furnace.

Using this technique, the final product retains, in most instances, the powdery texture of the original pure graphite substrate, but necessarily contains a certain amount of intercalated alkali metal in addition to the transition metal. An additional step, which has not been explored up to the present time, might be to completely remove all alkali metal from the catalyst by reaction with excess water or alcohol, followed by solvent removal. It is probable that somewhat different catalytic behavior would be observed for such materials due to the absence of alkali metal-graphites, which are themselves active for the Fischer-Tropsch synthesis (See Sub-Section C below). Pure alkali metal-graphites ($C_{64}Na$, C_8K, C_8Rb, and C_8Cs) are prepared using the same method, but eliminating the transition metal chloride intercalation step.

We have used the above-described technique to prepare intercalates of sodium and potassium for catalytic testing (Sub-Section C below), and have begun to apply it for the preparation of iron-graphite catalysts, on which we plan to focus most of our attention during the next quarter. We intend to prepare several samples of the latter over a 20-fold range of iron loading levels. Separate portions of each sample will be reduced with sodium and with potassium, and will be subsequently tested for catalytic activity and selectivity in the Fischer-Tropsch process. It is hoped that the data so obtained will provide general guidelines for future studies involving other transition metal-graphites.

C. Preliminary Catalytic Testing (Tasks 2a and 2b)

Because of the complex and ill-defined catalytic behavior of transition metal-graphites that retain intercalated alkali metal reducing agent, we have begun the catalytic testing segment of the project by examining in detail the activity and product selectivity exhibited by pure sodium and potassium graphites for the Fischer-Tropsch synthesis. The intent is to establish the individual catalytic properties of these materials in order that their contribution, if any, to the behavior of alkali-reduced transition metal-graphites can be recognized. This approach will enable meaningful conclusions to be drawn about the overall behavior of the multi-component catalysts. For comparison purposes, supplementary testing of a commercial supported iron catalyst has also been made. The latter was supplied by Harshaw Chemical Co. (Cat. No. FE-0301) as 20 wt% Fe_2O_3 on activated alumina, having a measured surface area of 45 m^2/g, and was reduced *in situ* in a stream of dry hydrogen for 6 hours at 300°C, following a 3 hour evacuation at 25°C.

All experiments reported below were performed using the reaction system described in Sub-Section A.2., and under identical reaction conditions, viz.:

Reaction Temperature : 300°C

Initial H_2/CO Ratio : 4/1

Initial Total Pressure : 750 torr

Total loaded catalyst weight in each case was 0.500 g (as 20 wt % Fe_2O_3 on alumina, or as pure graphite before intercalation of alkali metal). Absolute comparisons, however, of catalytic activity among the three types of catalysts described in the following Sub-Sections cannot be made because of the different total metal content in each catalyst. The primary intent of this preliminary testing was to establish relative product distributions that are obtained in each case.

1. Fe/Al_2O_3

Results obtained in a typical experiment with the supported iron catalyst are summarized in Table I, where distributions of carbon-containing products, percent conversions of CO, and carbon mass balances are presented as a function of reaction time. As expected for the relatively high-temperature, low-pressure conditions employed, the primary reaction products are dominated at all times by comparatively large and relatively constant amounts of carbon dioxide and methane, together with considerably lesser percentages of C_2, C_3, and C_4^+ paraffins and olefins. Conversion of carbon monoxide reactant increases fairly smoothly with reaction time, and the catalyst shows little time-dependent deactivation. The uniformly high (92-95%) gas-phase carbon balances indicate that little carbon monoxide is lost to the catalyst via irreversible adsorption and/or disproportionation, and, hence, that the observed carbon dioxide product is evidently not formed in significant amounts by the latter type of process, but is a true primary product of H_2/CO reaction. The gradually decreasing percentages of ethylene and propylene from high initial levels suggests their behavior as intermediates in the formation of ethane and propane via hydrogenation and C_4^+ formation via further chain growth.

The "used" catalyst could be regenerated by overnight evacuation at 300°C, followed by re-treatment with hydrogen, and results identical to those in Table I obtained upon repeating the synthesis reaction.

2. Sodium-Graphite ($C_{64}Na$)

Three consecutive runs were made using a single sample of sodium-graphite. The catalyst was "regenerated" between experiments by overnight evacuation at 300°C. The results are summarized in Table II. Although the data are complex, and certain inconsistencies exist among the three runs, several significant features of the overall catalytic behavior are apparent, Most notable among these is the complete absence of carbon dioxide from the reaction product in all cases. This phenomenon is quite unlike that observed with conventional supported metal catalysts (Table I) on which considerable amounts of carbon dioxide are normally formed under these reaction conditions. The behavior observed with sodium-graphite is due to the capability of alkali metal-graphites to reductively hydrogenate carbon dioxide to hydrocarbon products (U.S. Patent No. 3,842,113 (1974)). Thus, although carbon dioxide may form as a true primary reaction product, it quickly reacts further with hydrogen and does not appear among the gaseous product mixture.

The reaction product contains primarily C_1-C_3 paraffins in all cases, but considerable amounts of olefins and C_4^+ hydrocarbons are formed as well. The gradual decrease in the percentage of ethane with increasing reaction time and the simultaneous increase in methane content observed in the first and second runs are probably due to extensive hydrogenolysis of the C_2 paraffin caused by the relatively high H_2/CO reactant ratio employed. Overall conversion of carbon monoxide increases fairly rapidly during the first 2-5 hours, but changes only slightly thereafter. A considerable fraction of the high initial activity is recovered, however, following overnight evacuation at 300°C, as shown by the conversion levels obtained in the second and third runs.

A final important feature of the data for all runs is that a large percentage of the admitted carbon monoxide in each case becomes adsorbed on the catalyst in an apparently unreactive form, as evidenced by the low carbon mass balances observed. Disproportionation of carbon monoxide is an unlikely cause of this effect, but formation of a relatively stable carbonyl-type complex with the sodium-graphite matrix is a possible explanation. The latter phenomenon, however, cannot be verified at the present time. The presence of this inactive form of adsorbed carbon monoxide may be the reason for the observed decline in activity with increasing reaction time, as the "active" form pf CO becomes depleted. Evacuation at 300°C evidently removes the inactive species to a large extent and permits at least a partial recovery of catalytic activity.

3. Potassium-Graphite (C_8K)

A series of four consecutive experiments was performed using a single sample of potassium-graphite (C_8K) in a manner analogous to that described above for sodium-graphite, and the results are presented in Table III. Many of the overall features are, in general, similar to those observed in Table II, but certain important differences are apparent. Carbon dioxide was again absent, as expected, from the reaction product in all cases, but, more significantly, the hydrocarbon product distribution was confined almost exclusively to C_1-C_3 paraffins, and always in the relative order $C_2 > C_1 >> C_3$, the first two accounting for 95-98% of the observed product in every case. No evidence of ethylene or propylene was observed in any sample, and C_4^+ hydrocarbons were never present in more than trace amounts. Overall activity again declined after the first few hours of reaction, and an incremental decrease in initial activity was observed following each "regeneration", probably due to permanent destruction of metallic potassium by the water necessarily formed during reaction. A considerable fraction of admitted carbon monoxide was agian lost irreversibly to the catalyst, but the percentage of inactive CO declined with decreasing catalytic activity in successive runs, confirming that the strongly-adsorbed form of CO interacts in some manner with intercalated potassium atoms.

During the next quarter, we plan to complete our study of the individual catalytic behaviors of sodium- and potassium-graphites for the Fischer-Tropsch synthesis, and to begin catalytic testing of sodium- and potassium-reduced iron-graphites for this reaction. For comparative purposes, we also plan to examine the catalytic behavior of a commercially-available iron-graphite from Alfa Chemical Co. A spokesman for this company would not reveal the method used for iron reduction in preparing this material, but it definitely does not entail alkali metals, and probably consists of a treatment with sodium borohydride as the reducing agent. It is hoped that its behavior will be indicative of intercalated iron in the absence of alkali metals, and provide a possible alternative to complete removal of alkali metal via reaction with excess water or alcohol (Sub-Section B above).

IV. CONCLUSIONS

Procedures for preparing and handling alkali- and transition metal-graphites have been established, and samples of pure sodium- and potassium-graphites have been prepared for catalytic testing. Alkali metal-graphites exhibit catalytic properties for the Fischer-Tropsch synthesis that are quite unlike those of conventional supported transition metal catalysts. The most notable differences include a complete absence of carbon dioxide from the gaseous reaction product in all cases, and, in the case of potassium-graphite, exclusive confinement of the product distribution to C_1-C_3 paraffins. In addition, a considerable percentage of carbon monoxide reactant admitted to a fresh catalyst sample becomes irreversibly adsorbed in an unreactive form that may inhibit the overall reaction rate. The strongly-adsorbed CO is largely removed and activity partially restored by overnight evacuation at 300°C.

FIGURE 1

Project Plan and Progress Chart

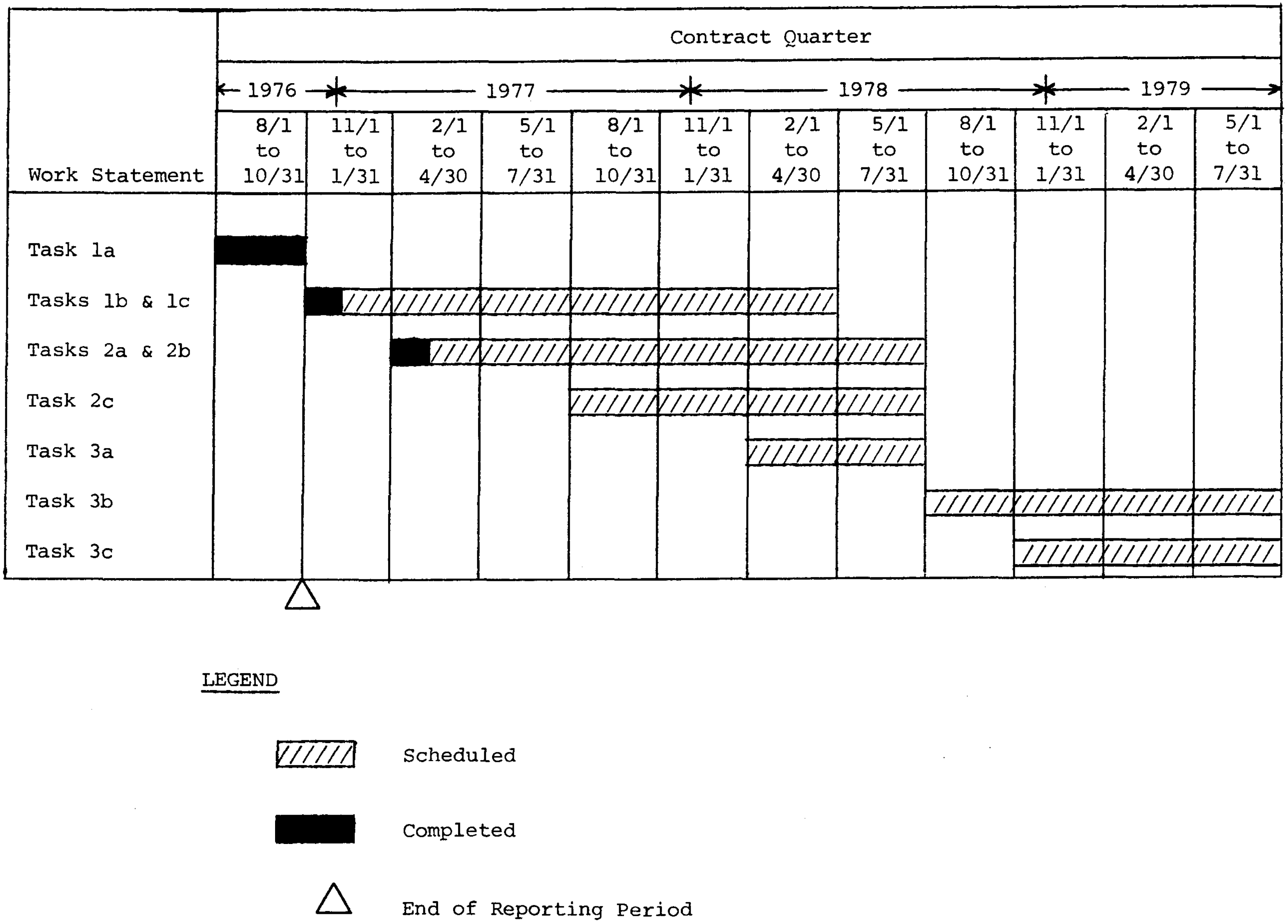

Table I

Fischer-Tropsch Synthesis on H_2-Reduced Fe_2O_3(20 wt%)/Al_2O_3

Reaction Temperature : 300°C
Initial H_2/CO Ratio : 4/1
Initial Total Pressure: 750 torr

Catalyst Wt.: 0.5 g (as 20 wt% Fe_2O_3/Al_2O_3
Reactor Vol.: 350 ml.

	Mole % in Gaseous Product								
Time (hr)	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4^+	% CO Conv.*	Carbon Balance* in Gas Phase
1	45.7	37.9	9.9	3.1	3.4	--	--	2.9	95
2	50.8	36.2	6.7	3.2	2.9	0.3	--	6.1	92
3	53.2	35.1	5.5	3.5	2.3	0.5	--	8.6	93
4	54.4	34.4	4.4	4.0	2.2	0.6	tr	10.9	93
5	55.4	33.8	3.7	4.2	2.1	0.7	tr	13.2	94
6	53.7	35.1	3.0	4.3	1.9	0.7	1.4	16.4	92
7	55.9	32.2	2.8	4.7	1.9	0.9	1.6	18.3	92
8	53.3	35.7	2.4	4.6	1.7	0.8	1.5	21.2	92
9	54.2	34.8	2.1	4.7	1.7	0.9	1.5	23.1	92
10	53.3	36.0	1.9	4.8	1.6	0.9	1.6	25.3	92

*Based on total CO admitted into reactor at time t=0

Table II

Fischer-Tropsch Synthesis on Sodium-Graphite ($C_{64}Na$)

Reaction Temperature : 300°C	Catalyst Wt.: 0.5 g (as graphite)
Initial H_2/CO Ratio : 4/1	Reactor Vol.: 350 ml.
Initial Total Pressure: 750 torr	

	Mole % in Gaseous Product								Carbon Balance*
Time (hr)	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4^+	% CO Conv.*	in Gas Phase
1	--	19.6	12.6	58.2	2.4	5.3	1.9	6.9	26
2	--	24.4	12.5	54.7	2.3	4.3	1.8	11.3	12
3	--	30.0	9.0	53.7	1.1	4.2	1.9	12.7	13
4	--	30.7	6.9	55.3	1.1	4.1	1.9	14.7	15
5	--	36.4	5.3	51.6	1.1	4.0	1.7	15.3	15
6	--	37.9	4.1	49.5	2.1	3.9	2.6	17.2	17
Evacuated 16 hrs at 300°C									
1	--	15.7	13.0	62.1	2.9	6.3	--	12.1	14
2	--	29.4	9.8	48.2	1.8	4.7	6.2	18.8	19
4	--	45.0	6.3	38.2	1.3	4.0	5.2	25.6	26
5	--	49.1	4.4	36.7	1.1	3.8	4.8	27.4	27
6	--	48.9	3.7	37.8	1.1	3.8	4.7	27.9	28
Evacuated 16 hrs at 300°C									
1	--	33.2	19.9	27.1	3.6	3.9	12.2	5.8	54
2	--	34.5	18.5	27.5	3.4	4.6	11.4	8.7	43
3	--	34.0	17.3	27.5	3.7	4.8	12.7	10.8	38
4	--	36.4	17.0	27.3	3.3	4.8	11.3	12.1	33
5	--	36.8	16.3	27.6	3.4	4.9	10.9	13.5	29
6	--	36.2	19.3	26.8	3.0	4.3	10.4	15.4	27
7	--	39.2	15.7	26.9	3.1	4.5	10.6	16.5	24
8	--	39.7	15.2	27.1	3.1	4.4	10.6	17.6	22
9	--	39.8	14.9	27.1	3.1	4.7	10.4	18.6	21

*Based on total CO admitted into reactor at time t=0

Table III

Fischer-Tropsch Synthesis on Potassium-Graphite (C_8K)

Reaction Temperature : 300°C
Initial H_2/CO Ratio : 4/1
Total Initial Pressure: 750 torr

Catalyst Wt.: 0.5 g (as graphite)
Reactor Vol.: 350 ml.

	Mole % in Gaseous Product								
Time (hr)	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4^+	% CO Conv.*	Carbon Balance* in Gas Phase
1	--	21.1	--	75.6	--	3.3	tr	18.5	21
2	--	24.3	--	72.3	--	3.4	tr	25.3	25
3	--	27.0	--	69.9	--	3.1	tr	28.7	29
4	--	28.4	--	68.4	--	3.2	tr	32.0	32
5	--	28.1	--	68.7	--	3.2	tr	34.0	34
6.3	--	29.2	--	67.8	--	3.0	tr	35.6	36
Evacuated 16 hrs at 300°C									
1	--	18.7	--	80.7	--	0.6	tr	12.1	36
2	--	25.2	--	73.1	--	1.6	tr	19.6	27
3	--	29.3	--	69.2	--	1.6	tr	25.6	28
4	--	28.5	--	70.0	--	1.5	tr	30.7	31
5	--	30.1	--	68.2	--	1.6	tr	33.0	33
Evacuated 16 hrs at 300°C									
1	--	19.9	--	78.3	--	1.8	--	5.0	65
2	--	29.8	--	68.9	--	1.3	--	6.4	54
3	--	30.2	--	67.3	--	2.5	--	6.8	50
4	--	31.2	--	67.1	--	1.7	--	7.0	46
Evacuated 16 hrs at 300°C									
0.5	--	~100	--	--	--	--	--	0.1	97
1	--	~100	--	--	--	--	--	0.2	97
2	--	~100	--	--	--	--	--	0.3	96

*Based on total CO admitted into reactor at time t=0