Table 2

MICROREACTOR
TEST PARAMETERS FOR FTS

Parameter	Range	Precision (%)
Catalyst weight	10 to 50 mg	± 1
Feed gas composition	5 vol% CO, 10 vol% H_2,* bal. He	± 1 vol %
Feed gas flow rate	10 to 600 cm^3/min	± 5
Pressure	100 to 120 kPa	—
Temperature	475, 500, 525, 550, 575 K	± 0.4
Co conversion	0.05 to 0.20 mol/mol feed	± 0.5
Product gas partial pressure CO, CO_2, C_1, C_5, C_6+	5 to 1000 Pa	± 5 (or ± 1 Pa)
CO conversion rate	0.4 to 400 μmol/g/s	± 10
CH_4 production rate	0.1 to 400 μmol/g/s	± 5
C_5 production rate	0.001 to 4 μmol/g/s	± 10

*H_2/CO ratio fixed at 2.00 ± 0.05.

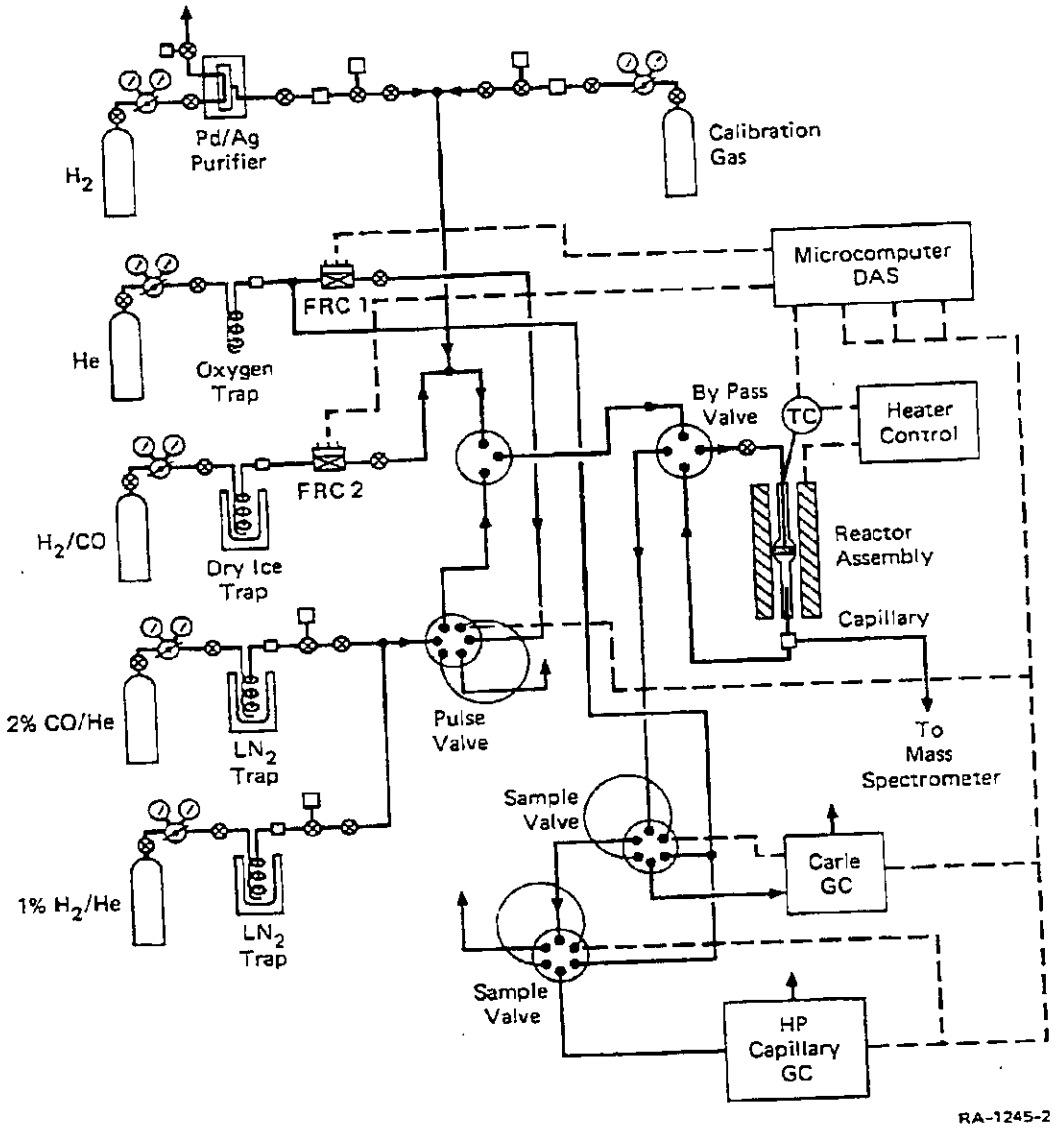

FIGURE 2 CATALYST CHARACTERIZATION AND FTS TESTING APPARATUS

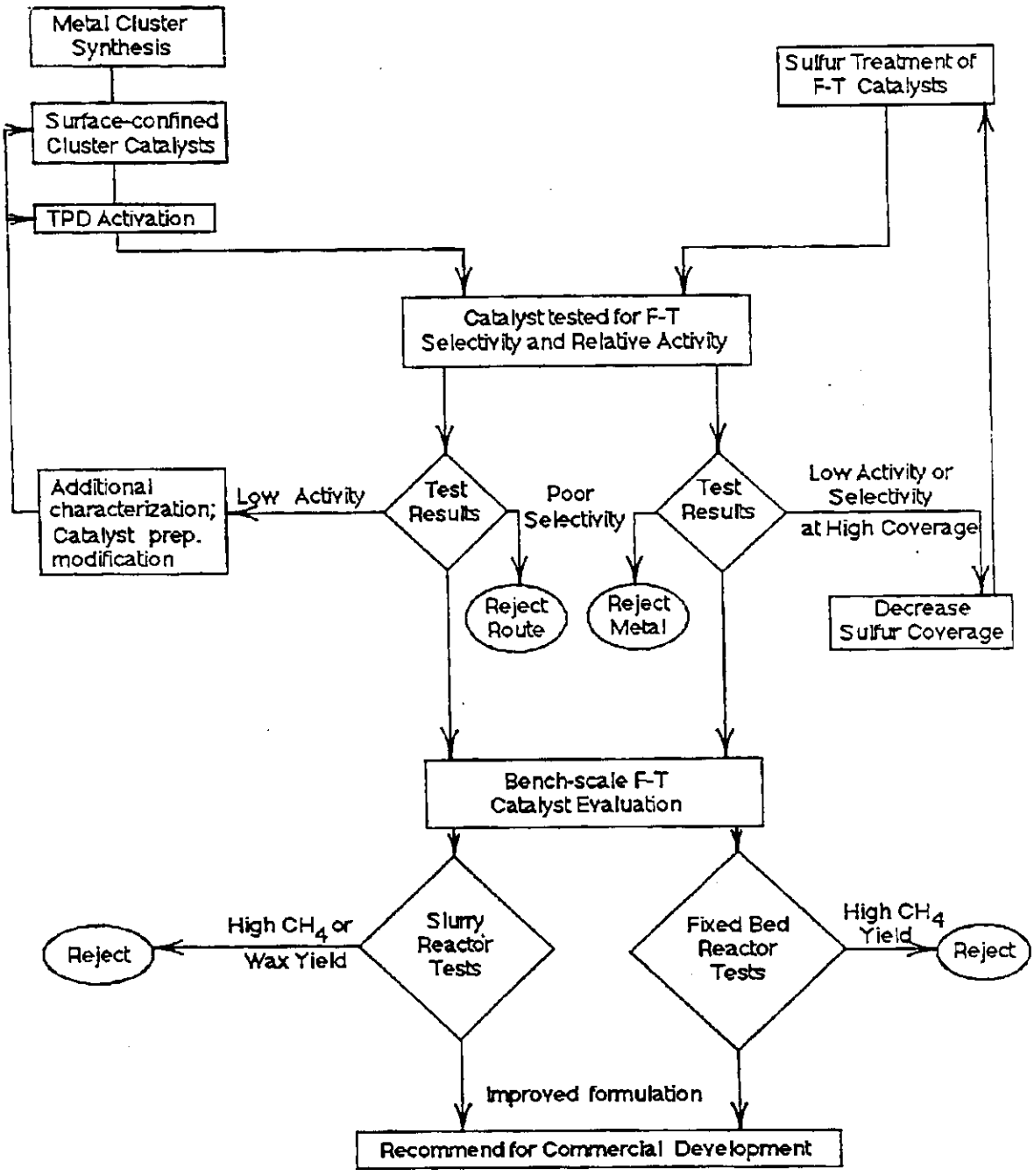

FIGURE 3 EXPERIMENTAL PROTOCOL

spectrometric analysis. The amount of the remaining allyl, ethyl, or carbonyl ligands will be of great importance in judging the kinetics and suitability of the various synthesis methods for the iron and Fe-Ru mixed-metal clusters, as well as providing information about the most appropriate activation procedures.

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. All these properties will be compared with those of the base catalyst under realistic FTS reactor conditions for an accurate gage of catalyst improvement. Detailed kinetic studies are not anticipated, although the effect of temperature and product gas partial pressure (such as CO_2 or H_2O) will be examined.

The two or three most promising improved FTS catalysts will be further evaluated, beyond the tests of Task 3, for activity and product distribution under 3.0 MPa pressure and inlet gas composition simulating purified syngas from a Lurgi oxygen-blown coal gasifier (50 vol.% H_2, 45 vol.% CO, and 5 vol.% CO_2). We anticipate using a semi-batch slurry reactor or a fixed-bed recycle reactor, depending on the properties of the improved catalyst.

For iron-based catalysts that require low temperatures (< 500 K) to achieve low methane selectivity, a semibatch slurry reactor (Autoclave Engineers) should best represent commercial operation. The syngas (containing variable levels of CO_2 if the catalyst is promoted) will flow through an agitated solvent (such as n-octacosane, C_{28}) containing the suspended finely powdered (< 50 μm) catalyst, and the effluent will be automatically sampled and analyzed by GC. The light gases—including hydrogen, methane, carbon monoxide, carbon dioxide, hydrogen sulfide, and light hydrocarbons (to C_6)—will be analyzed using a Carle automated two-column gas analyzer with TCD and FID detection. The heavier hydrocarbons will be analyzed using a temperature-programmable capillary column high-

resolution gas chromatograph (Hewlett-Packard 5890 with FID detector). See Figure 4 for a schematic diagram of the experimental apparatus. At the end of a run of up to 100 h under isothermal stationary state conditions, the liquid will be analyzed by HPLC[23] and periodically by field ionization mass spectrometry. The overall conversion rate and product distribution as a function of time will be determined for the fixed composition gas at several temperatures and space velocities. Table 3 gives a list of experimental parameters and specifications for this task.

Improved catalysts that can tolerate higher temperatures to reduce the formation of waxes may, on the advice and consent of the DOE project manager, be studied further in a fixed-bed internal recycle reactor in order to better simulate a fluid-bed reactor. The same experimental system and product gas analysis would be used as for the slurry reactor, with the exception of the reactor itself. The pressure and syngas composition will be as described above for the slurry reactor, but the temperature range will be higher (500 to 600 K). Rapid deactivation due to carbon deposition may be a problem at higher temperature. Therefore, at the end of a run, the catalyst will be removed and examined with temperature-programmed reaction (TPR) in hydrogen, oxygen, and helium, in a manner as described above for Task 3, to determine the quality and quantity of any carbonaceous residue.

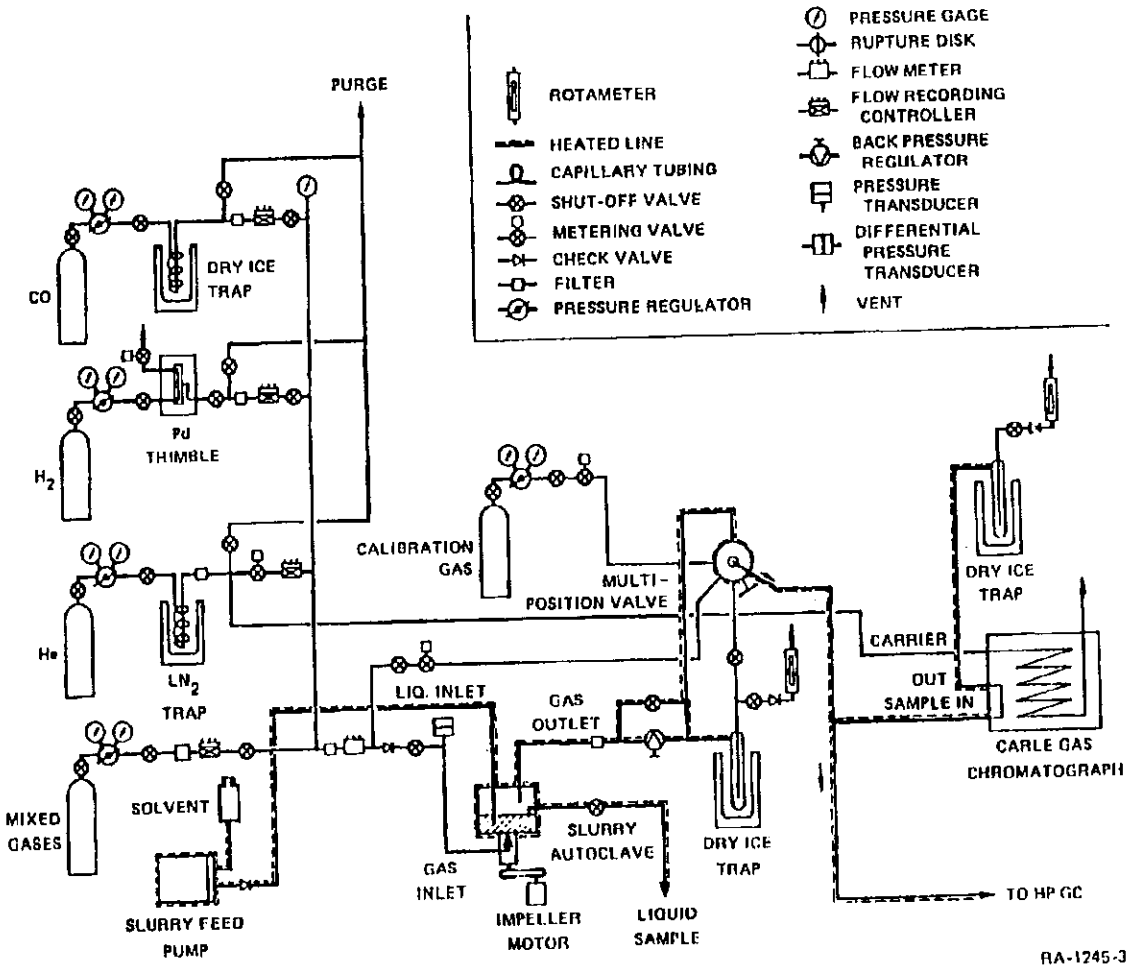

FIGURE 4 EXPERIMENTAL SYSTEM FOR FTS CATALYST EVALUATION

Table 3

EXPERIMENTAL PARAMETERS FOR FTS CATALYST EVALUATION

Parameter Description	Range	Accuracy (%)
General Parameters		
Pressure	3.0 Mpa	± 5
Feedgas Composition (H_2CO = 2.00 ± 0.05	CO_2 - 0.05 to 0.20 mol/mol feed [H_2 + CO] - 0.95 to 0.80 (bal)	± 3
Feedgas Flow Rate	1 to 25 x 10^{-6} m 3/s NTP	± 5
Per Pass CO Conversion	< 20%	-
Run Duration	2 to 50 h	± 1
Product Analysis (n = 2 to 30)	CO	± 3
	CO_2	± 5
	H_2	± 10
	CH_4	± 3
	C_nH_{2n+2}	± 5
	C_nH_{2n}	± 10
	$C_nH_{2n+1}OH$	± 10
Slurry Reactor Parameters		
Temperature	470 to 520 K	± 0.5
Volume of $C_{28}H_{58}$	0.5 to 2 x 10^{-3} m^3	± 10
Catalyst Load	1 to 20 g	± 0.1
Agitation Speed	50 to 300 rpm	± 10
Fluid-Bed Reactor Parameters		
Temperature	550 to 600 K	± 0.5
Catalyst Load	5 to 10 g	± 0.1
Agitation Speed	300 rpm	± 10

REFERENCES

1. G. Wilke et al., Angew. Cem. Int. Edit. 1/2, 151-266 (1966).

2. E. W. Abel and S. Moorhouse, J.C.S. Dalton 1973, 1706-1711.

3. A. C. Szary, S.A.R. Knox, and F.G.A. Stone, J.C.S. Dalton 1974, 662-664.

4. H. Foley, S. Delanio, K. Tao, K. Chao, J. Onoberko, C. Dybowski, and B. Gates, J. Am. Chem. Soc. 105, 3074-3082 (1983).

5. R. Pierantozzi, E. G. Valagene, A. F. Nordquist, and P. N. Dyer, J. Mol. Cat. 21, 189-202 (1983).

6. I. Boszormeryi, S. Dubes, K. Lazar, Z. Schay, and L. Guczi, Surface Sci. 156, 995-1002 (1985).

7. D. Rojas, P. Bussiere, J. A. Dalmon, A. Choplin, J. M. Basset, and D. Olivier, Surface Sci. 156, 516 (1985).

8. J. Bruno, J. Huffman, and K. Caulton, J. Am. Chem. Soc. 106, 444-445 (1984).

9. P. Budzelaar, K. den Haan, J. Boersma, G. van der Kerk, and A. Spek, Organometallics 3, 156-159 (1984).

10. P. Budzelaar, A. van der Zeigdon, J. Boersma, G. van der Kerk, A. Spek, and A. Duisenberg, Organometallics 3, 159-163 (1984).

11. A. de Miguel, M. Gomez, K. Isobe, B. Taylor, B. Mann, and P. Maitilis, Organometallics 2, 1724-1730 (1983).

12. C. N. Nagel and S. G. Shore, J.C.S. Chem. Comm. 1980, 530-531.

13. C. R. Eady, P. F. Jackson, B.F.G. Johnson, J. Lewis, M. C. Maletesta, M. McPartlin, and W.J.H. Nelson, J.C.S. Dalton 1980, 383-392.

14. D.B.W. Yawney and F.G.A. Stone, J. Chem. Soc. (A) 1969, 502-506.

15. G. L. Geoffroy, Acc. Chem. Res. 13, 469-476 (1980).

16. H. W. Walker, C. T. Kresge, P. C. Ford, and R. G. Pearson, J. Am. Chem. Soc. 101, 7428-7429 (1979).

17. R. D. Gonzales, Appl. Surface Sci. 19, 181-199 (1984).

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

19. J. G. McCarty and H. Wise, J. Chem. Phys. 74, 5877 (1981).

20. H. Wise, J. G. McCarty, and J. Oudar, "Sulfur and Carbon Interactions with Metal Surfaces," Chap. 1 in Deactivation and Poisoning of Catalysts, J. Oudar and H. Wise, Eds., Marcel Dekker (1985).

21. M. E. Dry and J. C. Hoogendoorn, Catal. Rev. 23, 265 (1981).

22. J. R. Rostrup-Nielsen, J. Catal. 21, 171 (1971).

23. G. A. Huff and C. N. Satterfield, J. Catal. 85, 370 (1984).

III PROJECT MANAGEMENT

Project Organization

Specific responsibility for the proposed research will reside in the Materials Research Laboratory (MRL), which is part of the Physical Sciences Division. Dr. D. L. Hildenbrand, Director of MRL, will be the Project Supervisor. All experimental work will be performed at SRI International, Menlo Park, California. SRI's Physical Sciences Division operates under a project management plan in which projects are reviewed on a regular basis by a selected group of management and senior professional personnel to ensure that all input necessary to a successful conclusion of the work is being provided. These management reviews will be an integral component of the overall management control of the proposed study, and associated costs have been included in the project cost estimate. The proposed project team and management structure are shown in Figure 5.

The project team for the proposed research program will include the following staff members:

- Dr. Jon G. McCarty, Manager of the Catalysis Program, is currently supervising research on several programs concerned with catalyst deactivation by sulfur and carbon deposition. He has studied the thermodynamics of sulfur deposition of catalysts, and he has extensive experience in catalyst activity measurements using various reactor configurations. Dr. McCarty will be the overall project leader and leader of Task 2.

- Dr. Robert B. Wilson, Jr., Organometallic Chemist, has extensive experience in homogeneous catalysis. In recent years he has studied catalyst systems composed of bimetallic cluster complexes, and he has investigated the immobilization of such clusters on solid supports. Dr. Wilson will lead Tasks 1 and 4.

- Mr. Bernard J. Wood, Senior Chemist, is currently studying the problem of catalyst deactivation by sulfur and carbon deposition on steam reforming catalysts. He has participated in catalyst studies at SRI for many years. He recently completed an investigation of the mechanism of catalytic gasification of coal char for DOE. Mr. Wood will lead Task 3.

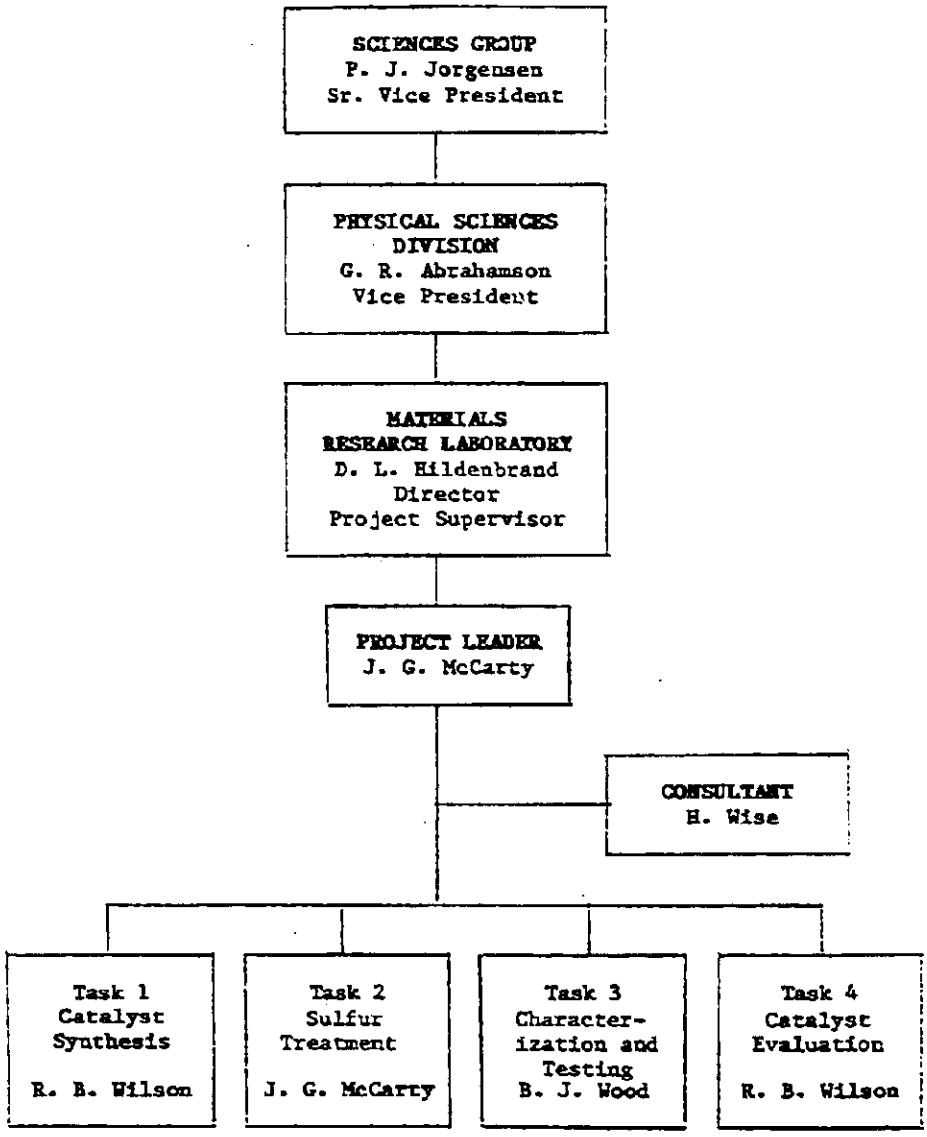

Figure 5. SRI Project Organization

- Mr. Michael Quinlan, Chemist, for a number of years has used the technique of temperature-programmed desorption/reaction to study the mechanism of catalyst action for a variety of reactions. Catalyst poisoning processes by sulfur and by halogens have been of particular concern in this work. Mr. Quinlan will assist in the characterization studies of Task 3.

- Mr. Gilbert Tong, Materials Chemist, is a chemical engineering graduate of the University of California at Berkeley. At SRI he has been engaged in studies of catalyst deactivation and catalytic coal gasification. Mr. Tong will assist in the reactor studies of Tasks 3 and 4.

- Dr. Hai Wei Huang, Postdoctoral Fellow, is an inorganic chemist recently graduated from Iowa State University. She has considerable experience in the synthesis of organometallic complexes. Dr. Huang will perform the organometallic synthesis reactions of Task 1 and assist in the evaluation studies of Task 4.

In addition to this research team, the following staff member will serve as consultant to the program:

- Dr. Henry Wise, Scientific Fellow, directed catalysis research at SRI for many years. He has made numerous contributions to the field of catalysis, as exemplified by more than 100 publications in books and scientific journals. Recently, he has been involved in studies of catalyst deactivation by sulfur and carbon.

Project Schedule

A detailed program schedule for the project, broken down into estimated time for completion of each task and report, is given in Figure 6. Results from the activation and characterization tests, conducted in Task 3 (which will run parallel to Tasks 1 and 2), may result in modifications in synthesis procedure, abandonment of a synthesis route, or more emphasis on a route that shows promise. Similarly, the sulfur treatment task, Task 2, may also be modified based on the results of the testing. For example, if half- saturation with sulfur leads to a catalyst with very poor activity, additional tests with sulfur coverage greater than half-saturation will be abandoned.

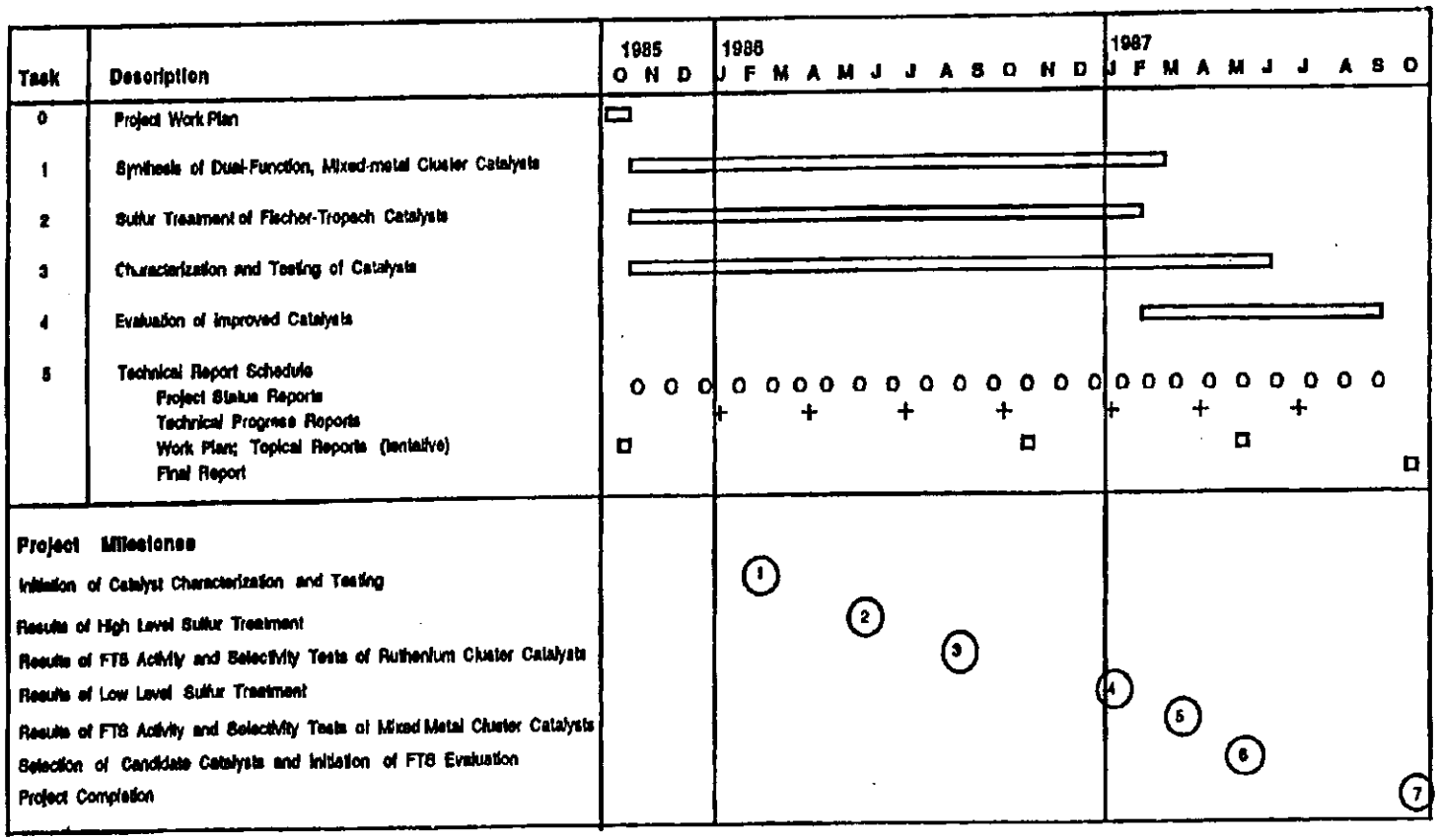

Figure 6. Program Schedule and Milestone Chart

Estimated Labor Hours

As discussed above, each task requires contributions from several staff members. In a research program of this type, it is not possible to identify the number of labor hours each staff member will spend on each aspect of the program. However, on the basis of our past experience with similar programs we have estimated the number of labor hours, by labor category, required for each task, and these are shown in Table 4. Some of the supervisory personnel, in addition to their supervisory function, will participate in the technical performance of the program. The professional staff will perform the necessary experimental work and will assist supervisory and senior staff in the performance of other tasks. The estimated fraction of time the key personnel will devote to each task listed in Table 5.

Cost Management

The materials and supplies cost estimates (Table 6) for project 1245 are attached below. The Cost Plan (DOE Form CR-533P, Table 7) was derived from the cost estimate schedules of our proposal PYU-127R dated August 29, 1985, with adjustments for the increase in M&S costs (due to a more detailed cost breakdown) and the final contract size, $289,007 vs. $290,397 as proposed. The initial Contract Management Summary Report (DOE Form 536) is also attached (Table 8).

Government Property

We do not expect to purchase capital equipment for project 1245. Government property presently located at SRI International may be required for use in Task 4. SRI will formally request the transfer of such equipment as needed and according to the conditions of our contract.

Table 4

ALLOCATION OF LABOR HOURS BY TASK

Task Description	Supervisory	Senior Professional	Professional	Clerical, Technical, and Report	Total
0. Work Plan	40	0	40	42	122
1. Synthesis of Dual-Function Mixed-Metal Cluster Catalysts	6	0	1611	21	1638
2. Sulfer Treatment of Fischer-Tropsch Catalysts	222	0	570	39	831
3. Characterization and Testing of FTS Catalysts	6	378	1117	39	1540
4. Evaluation of Improved FTS Catalysts	6	0	798	21	825
5. Report Production and Travel	40	42	216	372	690
Total	320	420	4352	534	5646

Table 5

ESTIMATED FRACTIONAL* TIME COMMITMENT

Task No.	Task Duration (weeks)	J. G. McCarty	R. B. Wilson	B. J. Wood	H. W. Huang	M. A. Quinlan	G. Tong	Clerical	Technical	Report
0	4	25	25	5	0	0	0	15	0	12
1	80	0	10	0	45	0	0	0	1	0
2	76	10	0	0	0	0	15	0	1	0
3	88	10	0	12	0	5	15	0	1	0
4	32	1	8	0	45	0	0	0	2	0
5	100	1	2	1	5	1	1	5	0	5

*Expressed as the % of personnel time charges devoted to each task.

Table 6

ESTIMATED COSTS FOR MATERIALS AND SUPPLIES

	Description	Estimated Cost $
TASK 1:	reagents for organometallic synthesis	600
	organometallic catalysts	400
	glassware	300
	gases (dry N_2)	60
	dry ice, liquid nitrogen	200
	miscellaneous supplies	240
		$1700
TASK 2:	reagents for catalysts	100
	carrier gases (He, H_2)	60
	mixed gases (H_2S/H_2, CO/He)	180
	oxytraps (2)	60
	sieve traps (2)	60
	dewars for traps (2)	60
	in-line filters	60
	TFE fittings	200
	VCO fittings	200
	pump diaphram	100
	H_2S/H_2 regulator	100
	solid-state relays	100
	sampling valves (2)	800
	valve actuator	200
	miscellaneous supplies	240
		$2800
TASK 3:	carrier gases (He, H_2)	90
	mixed gases ($CO+H_2$, CO+He)	250
	liquid nitrogen	800
	VCO fittings	300
	SS fittings	300
	TFE fittings + quartz for reactors	300
	cut-off isolation valves (4)	180
	sampling valve	400
	valve actuator	200
	miscellaneous supplies	140
		$2900

TASK 4:	back pressure regulators (2)	800
	sampling valves (2)	800
	metering valves	300
	SS fittings & tubing	600
	carrier gases (H_2, He)	120
	mixed gases (CO + H_2, CO_2)	400
	liquid nitrogen + dry ice	100
	DAS interface components	300
	miscellaneous supplies	380
		$3700
	Total Materials and Supplies	$11,100