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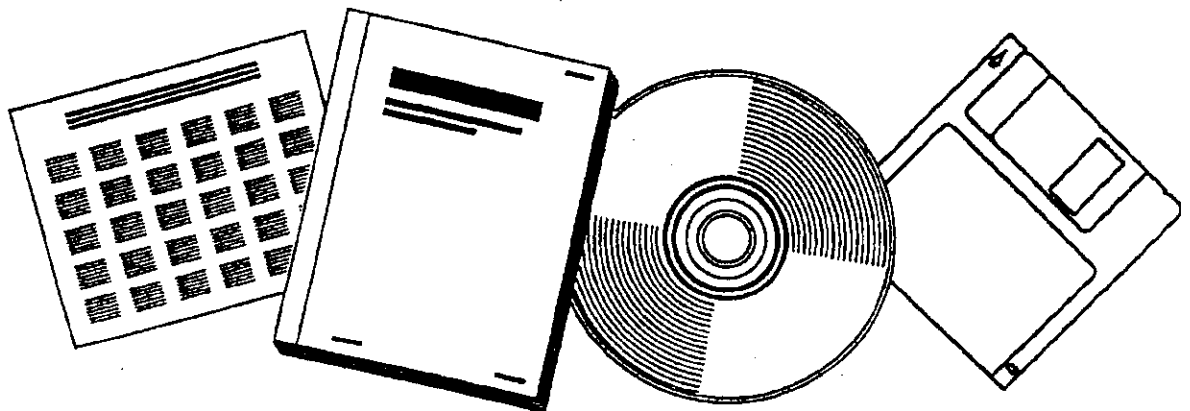
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**IMPROVED FISCHER-TROPSCH SYNTHESIS  
CATALYSTS FOR INDIRECT COAL LIQUEFACTION.  
TOPICAL REPORT NO. 1: THE PROJECT WORK  
PLAN**

SRI INTERNATIONAL  
MENLO PARK, CA

15 NOV 1985



**U.S. DEPARTMENT OF COMMERCE**  
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November 15, 1985

IMPROVED FISCHER-TROPSCH SYNTHESIS CATALYSTS  
FOR INDIRECT COAL LIQUEFACTION

Topical Report No. 1 - The Project Work Plan

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#### ABSTRACT

This report represents completion of Task 0, the project work plan, required by DOE prior to initiation of SRI's experimental research program. The work plan consists of a detailed narrative of the experimental program, the estimated project schedule, and various charts and tables describing the project organization and cost management.

The goal of SRI's research program is to narrow the FT product distribution through two methods of catalyst development. The first approach consists of the organometallic synthesis of multiatomic ruthenium and iron-ruthenium alkyl-carbonyl clusters, the reaction of these clusters with acidic alumina or silica-alumina supports and the activation and characterization of these surface-confined clusters by temperature programmed decomposition and infrared spectroscopy. This method will focus on the development of very active FT catalysts with low wax yield. In the second approach, conventional promoted and unpromoted Fe, Co, and Ru catalysts will be treated by uniform deposition of low submonolayer levels of chemisorbed sulfur. This method will focus on selectively suppressing methane production. Catalysts developed by both methods will be given common characterization measurements and tested for their catalytic activity and FT product distribution relative to a standard precipitated iron catalyst. Those catalysts that promise significant improvement in selectivity will be further evaluated in bench-scale laboratory tests under realistic FT reactor conditions.

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## I INTRODUCTION

The goal of this research project is to develop Fischer-Tropsch synthesis (FTS) catalysts with high activity and improved product selectivity. Two approaches to catalyst development will be investigated.

The first approach is an organometallic synthesis approach consisting of (i) the synthesis of multiatomic ruthenium and iron-ruthenium alkyl-carbonyl clusters, (ii) the bonding of these clusters by reaction with Bronsted acid sites on alumina or silica-alumina supports, and (iii) the activation and characterization of these catalysts by temperature-programmed desorption, infrared spectroscopy, and activation analysis (AA). The effect of such very high dispersion on FTS selectivity is not established; however, based on reports in the current literature, we expect a decrease in high molecular weight hydrocarbons. If these catalysts have high activity and low wax yield, they may be excellent candidates for improved FTS catalysts for slurry reactors.

In the second approach, we will attempt to selectively poison promoted and unpromoted iron, and supported cobalt and ruthenium catalysts with low-level sulfur chemisorption. We expect to thereby selectively poison those sites or intermediates responsible for methane production with a lesser effect of such poisoning on higher hydrocarbon yield. If selective poisoning can be accomplished, these catalysts may be useful as improved catalysts for slurry reactors. If the FTS activity is low, they may be useful at higher temperature for fluidized bed reactors.

The catalysts prepared by both approaches will be given specific characterization tests and then evaluated for surface area, FTS activity, and FTS selectivity relative to precipitated iron in a fixed-bed microreactor system. The results of these tests will be used to guide

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further catalyst synthesis and catalyst treatment efforts and to select the best improved catalyst candidates for a more detailed investigation of FTS activity, stability, product selectivity, methane yield, and wax accumulation.

This report represents completion of Task 0, the project work plan. We begin with a detailed discussion of the experimental methods and technical approach of the individual tasks. The project management is then presented, including personnel data, the program schedule, project work chart, and cost management.

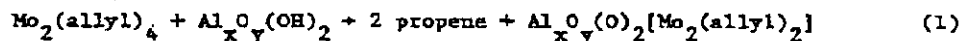
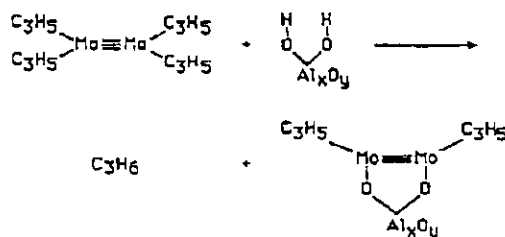
## II TECHNICAL APPROACH

The contractual Statement of Work is attached as Appendix A. The technical approach and methods used in Tasks 1 through 4, comprising the experimental program, are discussed below.

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

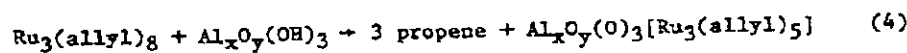
Surface-confined FTS catalysts will be synthesized using a pendant hydrocarbyl functional group that reacts with the hydroxyl groups on the surface of a support material. Experimental variables affecting synthesis of the catalysts include the cluster size and composition and the nature of the support. Initially, alumina will be used as the support; later support materials may include highly acidic  $\text{SiO}_2\text{-Al}_2\text{O}_3$  synthetic zeolites and shape-selective high-silica zeolites.

The preferred method of preparation is by reaction of metal hydrocarbyls with surface hydroxyl groups on the support, as shown in reaction (1).

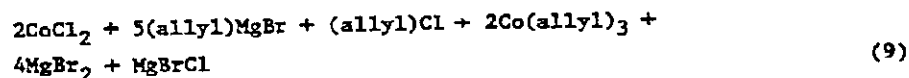
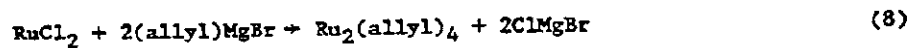
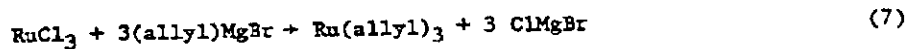
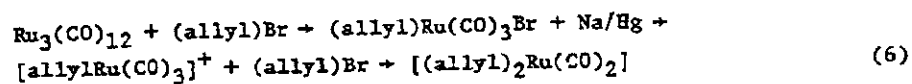
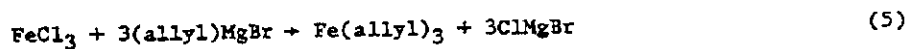




Reactions such as (1) are well understood and generally rapid (even below room temperature), and the resulting surface-confined metal hydrocarbyls generally have extremely low activation temperatures.  $\text{Fe(allyl)}_3^1$  or  $\text{Ru(allyl)}_2(\text{CO})^2$  are known compounds that could be used directly. It may also be possible to synthesize  $\text{Ru(allyl)}_3$ ,  $\text{Ru}_2(\text{allyl})_4$ , or  $\text{Ru}_2(\text{allyl})_6$ , and  $\text{Ru}_3(\text{allyl})_8$  complexes based on the known cycloheptatrienyl,  $\text{C}_8\text{H}_{10}\text{Ru}_2(\text{CO})_6^3$ , and cyclooctatrienyl,  $(\text{C}_8\text{H}_8)_2\text{Ru}_3(\text{CO})_4$ , compounds. The cycloheptatrienyl and the cyclooctatrienyl ligands act as bis(allyl) ligands, bridging two metals. Surface-confined mono-, di-, and trinuclear ruthenium species could be prepared according to the following set of reactions:



The allyl complexes to be used will be synthesized by the following routes:



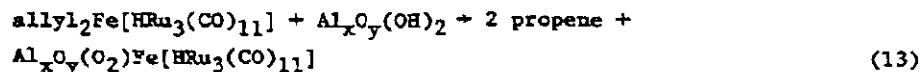
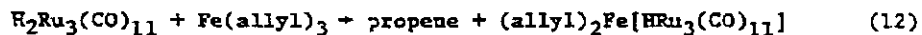
The Fe and Co trisallyl complex (and most likely both ruthenium allyl complexes) are thermally unstable so that the subsequent reaction [e.g., reaction (2) or reaction (12) below] must be conducted at low temperature immediately following the preparation of these complexes.

The stability of surface-confined ruthenium carbonyl clusters has been questioned by Gates<sup>4</sup> and Pierantozzi<sup>5</sup>, among others.<sup>6,7</sup> To prepare a catalyst having a surface binding that is better characterized and stronger than the normal surface-confined carbonyls, we propose to study the use of pendant group surface confinement as shown in reactions (10) and (11).



Reactions of alkyl aluminum or zinc compounds with transition metal hydrides has recently been reported by two groups.<sup>8-11</sup> Using this method, we can bind the cluster, even multiple clusters, to the same site. It is likely that under FTS reaction conditions, the Al-Ru bonds will be transformed into support metal interactions and the Al will undergo oxidation.

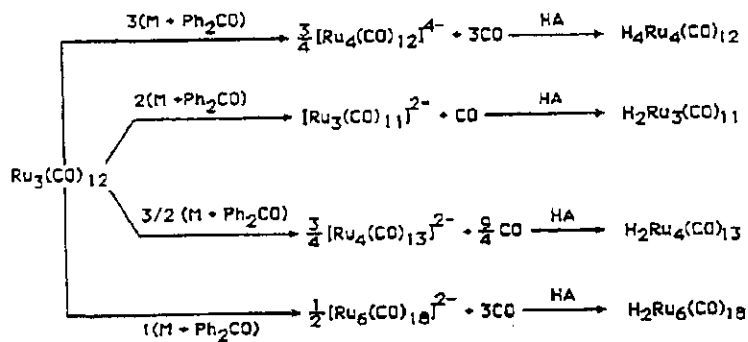
This synthesis concept can be extended to eliminate the need to introduce Al-Ru bonds into the surface-bound cluster. If we substitute  $\text{Co}(\text{allyl})_3$ <sup>1</sup>,  $\text{Fe}(\text{allyl})_3$ ,  $\text{Ru}(\text{allyl})_2(\text{CO})_2$ , or  $\text{Ru}(\text{allyl})_3$  for the  $\text{Et}_3\text{Al}$ , we have the following reactions:



Potential hydrido ruthenium carbonyl clusters include  $\text{H}_2\text{Ru}_3(\text{CO})_{11}$ ,  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ ,  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ , and  $\text{H}_2\text{Ru}_6(\text{CO})_{18}$ .<sup>12,13</sup> Potential mixed-metal hydrido ruthenium/iron carbonyl clusters include  $\text{H}_2\text{FeRu}_2(\text{CO})_{11}$ ,  $\text{H}_2\text{RuFe}_2(\text{CO})_{11}$ ,  $\text{H}_4\text{Ru}_3\text{Fe}(\text{CO})_{12}$ , and  $\text{H}_4\text{Ru}_4\text{Fe}_2(\text{CO})_{12}$ .<sup>14,15</sup> The use of these eight compounds and appropriate metal allyls—such as  $\text{Al}(\text{allyl})_3$ ,  $\text{Fe}(\text{allyl})_3$ ,  $\text{Ru}(\text{allyl})_2(\text{CO})_2$ ,  $\text{Ru}(\text{allyl})_3$ , and  $\text{Co}(\text{allyl})_3$ —will allow us to determine the optimum method of preparation, the most effective composition of metals (Fe, Ru, and Co), and the preferred cluster size. We expect that for our initial studies, we will use a range of 1-7 metal atoms per cluster.

The hydrido ruthenium carbonyl clusters will be synthesized by the method of Shore.<sup>12,13</sup>  $\text{Ru}_3(\text{CO})_{12}$  reacts with sodium benzophenone in THF. By careful control of the stoichiometry, it is possible to prepare the anions of all four of the ruthenium clusters. The anions will be carefully treated with acid to give the hydrido clusters, Scheme I.

Scheme I

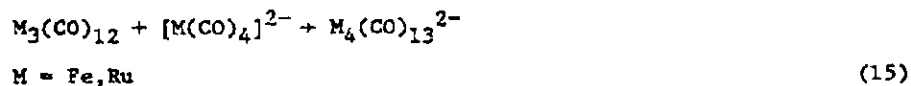


M = K, Na, Li

The mixed metal clusters will be prepared by the method of Stone:<sup>14</sup>



The tetranuclear clusters will be prepared by the method of Geoffroy<sup>5,15</sup> which entails the addition of a mononuclear anion to the trinuclear cluster.



It is important to emphasize that all the metal hydrides cited thus far are, in fact, more acidic than H<sub>2</sub>O and will react rapidly with the aluminum alkyl and ruthenium allyl compounds<sup>16</sup> according to reactions (10) and (12), respectively.

The isolated complexes will be synthesized and stored (at subambient temperatures if necessary) in a dry box. Selected complexes will be characterized by FTIR, FTNMR, and elemental (AA) analysis.

The reaction of the metal hydrocarbyls with the hydroxyl groups on an alumina surface will be followed by measuring the evolved gas. The volume of the gas will be measured by mercury monometer and the composition will be determined by gas chromatography. The metal loading will be determined by AA. The reaction will also be followed by observing changes in the IR spectra taken in the diffuse reflectance mode on our Digilab FTS-20E FTIR. The supported clusters will be further characterized in Task 3, with one addition—after each activation or FTS test, the selected spent catalysts will be isolated and their FTIR spectra will be determined for comparison with the FTIR of the fresh catalysts. Techniques for characterization of these catalysts have been the subject of a recent critical review article by Gonzales.<sup>17</sup>

## Task 2 - Sulfur Treatment of Fischer-Tropsch Catalysts

Low-level sulfur-treated iron, cobalt, and ruthenium catalysts will be prepared for subsequent characterization and measurements of FTS activity and selectivity. The goal of the task is to selectively deposit sulfur at ledge sites or on open crystal faces—for example, Fe(111)—that have the greatest affinity for sulfur adatoms while leaving the majority of the surfaces uncovered. However, work performed previously in our laboratory<sup>18,19</sup> has shown the equilibrium partial pressure ratio of H<sub>2</sub>S to H<sub>2</sub> required for less than half-saturation coverage falls on iron and cobalt powders well below practical levels.

The key technical difficulty of this task will be to uniformly adsorb sulfur on the reduced metal surfaces at a fraction of the saturation coverage. At typical reduction temperatures (623 K), the reversible gas phase concentration of H<sub>2</sub>S in hydrogen will be well below 1 ppb (Table 1). Modified Tempkin adsorption equations describing sulfur chemisorption on iron and cobalt powders and alumina-supported ruthenium have been determined<sup>20</sup> and will be used to guide the procedures of Task 2. The thermodynamic results suggest that during most previous sulfur poisoning experiments involving FTS, the catalysts were not uniformly poisoned, and that our efforts to achieve uniform sulfur coverage throughout a catalyst particle and the catalyst bed at low levels will be difficult.

Several different methods of uniformly adsorbing sulfur may be required, depending on the level of coverage. For coverage at or above half-saturation, a recirculating gas system (Figure 1) will be used in which the desired amount of sulfur is introduced into a closed recirculating hydrogen stream and allowed to equilibrate. Our experience with equilibrium measurements of sub-ppm concentrations of H<sub>2</sub>S for reversible sulfur chemisorption on supported metals has shown that careful selection of materials (quartz, polyfluorocarbons, and polyethylene) and cleaning are required. Also, the process of uniform adsorption may require days if the H<sub>2</sub>S level falls below 10 ppb. Lower coverage cannot be achieved unless the catalyst is heated to very high temperatures (above 800 K), where sintering may seriously degrade the FTS activity.

Table 1

Metal	Temp (K)	PH <sub>2</sub> S/PH <sub>2</sub> for Fractional Sulfur Coverage, θ <sub>s</sub>					
		0.05	0.10	0.20	0.50	0.75	1.00
Fe	500	6.6 x 10 <sup>-15</sup>	1.3 x 10 <sup>-14</sup>	2.7 x 10 <sup>-14</sup>	5.4 x 10 <sup>-11</sup>	3.6 x 10 <sup>-8</sup>	2.1 x 10 <sup>-5</sup>
	600	6.4 x 10 <sup>-13</sup>	1.3 x 10 <sup>-12</sup>	2.5 x 10 <sup>-12</sup>	2.6 x 10 <sup>-9</sup>	8.9 x 10 <sup>-7</sup>	2.8 x 10 <sup>-4</sup>
	800	1.9 x 10 <sup>-10</sup>	3.8 x 10 <sup>-10</sup>	7.6 x 10 <sup>-10</sup>	3.2 x 10 <sup>-7</sup>	4.9 x 10 <sup>-5</sup>	6.8 x 10 <sup>-3</sup>
	1000	5.8 x 10 <sup>-9</sup>	1.2 x 10 <sup>-8</sup>	2.3 x 10 <sup>-8</sup>	5.7 x 10 <sup>-6</sup>	5.5 x 10 <sup>-4</sup>	4.7 x 10 <sup>-2</sup>
Co	500	6.1 x 10 <sup>-16</sup>	1.2 x 10 <sup>-15</sup>	2.4 x 10 <sup>-15</sup>	1.8 x 10 <sup>-12</sup>	3.5 x 10 <sup>-10</sup>	6.1 x 10 <sup>-8</sup>
	600	1.8 x 10 <sup>-13</sup>	3.6 x 10 <sup>-13</sup>	7.3 x 10 <sup>-13</sup>	2.1 x 10 <sup>-10</sup>	1.8 x 10 <sup>-8</sup>	1.4 x 10 <sup>-6</sup>
	800	2.3 x 10 <sup>-10</sup>	4.5 x 10 <sup>-10</sup>	9.0 x 10 <sup>-10</sup>	7.9 x 10 <sup>-8</sup>	2.5 x 10 <sup>-6</sup>	6.9 x 10 <sup>-5</sup>
	1000	1.6 x 10 <sup>-8</sup>	3.2 x 10 <sup>-8</sup>	6.5 x 10 <sup>-8</sup>	2.8 x 10 <sup>-6</sup>	4.8 x 10 <sup>-5</sup>	7.2 x 10 <sup>-4</sup>
Ru	500	2.3 x 10 <sup>-26</sup>	4.3 x 10 <sup>-25</sup>	1.5 x 10 <sup>-22</sup>	7.0 x 10 <sup>-15</sup>	1.7 x 10 <sup>-8</sup>	4.1 x 10 <sup>-2</sup>
	600	3.4 x 10 <sup>-23</sup>	5.1 x 10 <sup>-22</sup>	1.2 x 10 <sup>-19</sup>	1.4 x 10 <sup>-12</sup>	1.1 x 10 <sup>-6</sup>	9.0 x 10 <sup>-1</sup>
	800	3.1 x 10 <sup>-19</sup>	3.5 x 10 <sup>-18</sup>	4.7 x 10 <sup>-16</sup>	1.1 x 10 <sup>-9</sup>	2.1 x 10 <sup>-4</sup>	4.2 x 10
	1000	7.3 x 10 <sup>-17</sup>	7.1 x 10 <sup>-16</sup>	6.7 x 10 <sup>-14</sup>	5.7 x 10 <sup>-8</sup>	4.9 x 10 <sup>-3</sup>	4.3 x 10 <sup>2</sup>

Source: J. Chem. Phys. 74, 5877 (1981); J. Chem. Phys. 76, 1162 (1982).

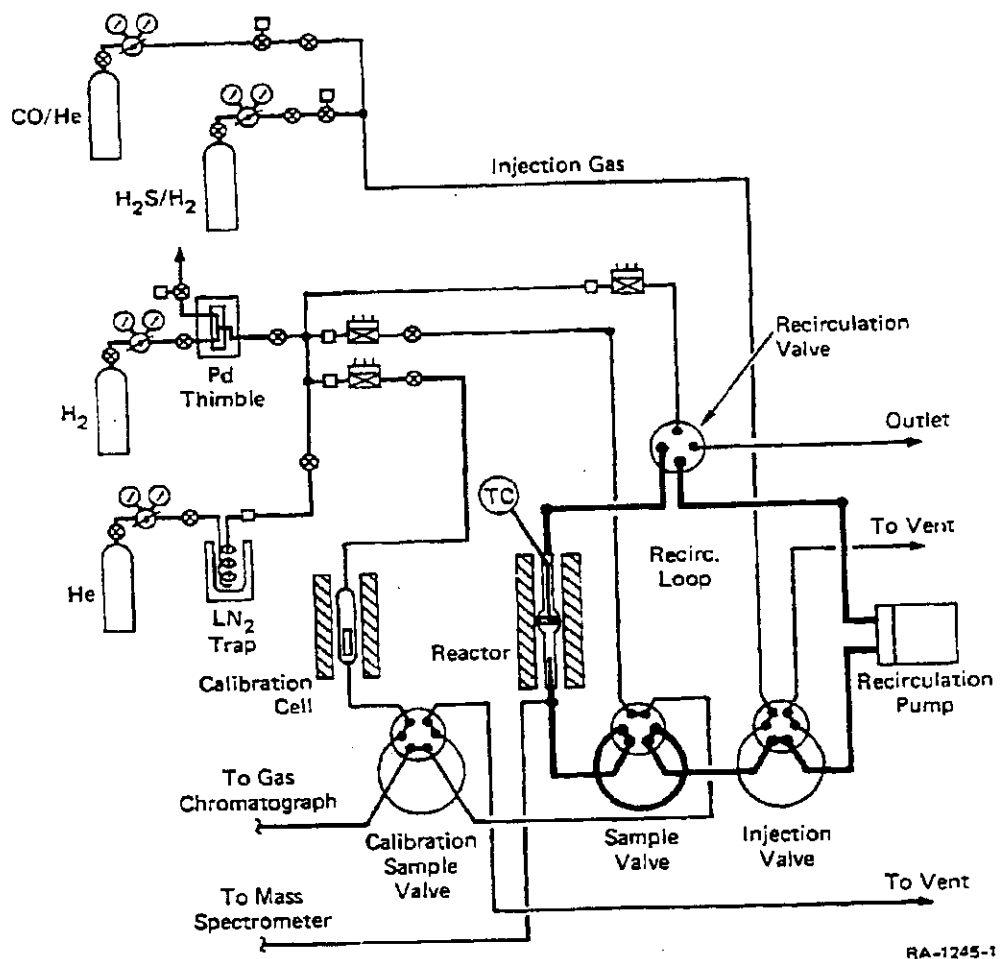


FIGURE 1 FTS CATALYST SULFUR TREATMENT SYSTEM

An alternate approach for uniform sulfur adsorption will be attempted for fractional coverage well below half the saturation coverage. The method is based on impeding the dissociative chemisorption of the  $H_2S$  to achieve the desired overall level of sulfur coverage. Uniform adsorption would occur if the rate of sulfur chemisorption were limited by surface reaction rather than pore diffusion. The reduced metal surfaces will be passivated by carbon deposition, the initial growth of iron carbide by CO adsorption, dissociation, and disproportionation to  $CO_2$ . The partial pressure of CO will be kept at approximately 0.1 to 1 kPa in the 100-kPa helium circulation gas stream by injection of aliquots of 10 kPa CO in 90-kPa He. The catalyst temperature will range from 350 to 550 K, and attempts will be made to control carbon deposition to a few monolayers by measuring the production of  $CO_2$ . With 1 kPa CO present in the recirculating gas to further impede adsorption, aliquots of  $H_2S$  will be injected representing 0.05 to 0.25 monolayer sulfur capacity. The rate of  $H_2S$  adsorption will be controlled to about 0.1 monolayer per hour by adjusting the catalyst temperature from 250 to 500 K while monitoring the decrease in gas phase  $H_2S$  concentration.

Once sufficient  $H_2S$  has irreversibly adsorbed, the system will be flushed with pure  $H_2$  at 300 K. The carbon and adsorbed CO will be removed by slowly heating the catalyst to temperatures as high as 873 K in 100-kPa flowing  $H_2$ . The gas stream will be analyzed to monitor the carbon removal as  $CH_4$  and to check for loss of  $H_2S$ , although we expect no loss of sulfur. The catalyst will be held in 100 kPa  $H_2$  under recirculation at 873 K for at least 10 h to allow local microscopic surface diffusion and gas-surface transport to occur so that the sulfur adatoms will find and occupy only high-coordination adsorption sites on the metallic surfaces.

Alternative passivation schemes may be attempted if the carbon/CO system just described fails. These may include carbon/ $C_2H_4$ , oxygen/ $H_2O$ , or nitrogen/ $NH_3$ . A low-level sulfur treatment process will be considered successful if the rate of sulfur chemisorption can be controlled at low temperature and the sulfur treatment is irreversible during removal of the passivating element.



Following pretreatment, the catalyst will be characterized by CO adsorption at  $325 \pm 25$  K, passivated by CO chemisorption, and transferred to the microreactor system described in Task 3 for tests of FTS activity and selectivity.

The catalysts to be examined in this task include the precipitated iron standard, a fused iron catalyst, a precipitated Fe-Cu-SiO<sub>2</sub> catalyst, and Ru/Al<sub>2</sub>O<sub>3</sub> and Co/Al<sub>2</sub>O<sub>3</sub> catalysts. The effect of sulfur pretreatment on potassium-promoted iron catalysts will be determined as well. Sulfur coverages at approximately 10% of saturation or less, half-saturation, and 75% to full saturation (relative to 1 ppm H<sub>2</sub>S in H<sub>2</sub> at 573 K) will be used to provide a representative range for the kinetic tests. The precipitated Fe catalyst will be treated by sulfur chemisorption over the full range of coverage; the other catalysts will be initially treated to approximately half saturation. Those catalysts for which half-saturation sulfur coverage produces good results (i.e., decreased methane selectivity) will be tested following treatment for still lower fraction sulfur coverage.

The precipitated iron catalyst, the base catalyst, will be prepared by mixing a solution of high purity nitrate into an agitated boiling sodium carbonate solution. The resulting precipitate will be washed in hot distilled water to remove the sodium, rinsed with high purity acetone to reduce the water content, and oven-dried in air. Before use, the precipitated iron oxide will be reduced in stages in flowing H<sub>2</sub> at 373 K, 523 K, and 673 K, for at least 30-minutes duration per stage. Potassium can be added by impregnation of the dried precipitated oxide with potassium hydroxide or carbonate using the incipient wetness technique. The Fe-Cu-SiO<sub>2</sub> catalyst will be prepared in a similar fashion with 5 wt% copper nitrate, and the addition of potassium waterglass to the Fe<sub>2</sub>O<sub>3</sub> slurry.<sup>21</sup> The Co and Ru catalysts will be prepared using the impregnation-incipient wetness technique with nitrate salts and a moderate surface-area alumina. The fused iron catalyst will be either obtained from vendors or prepared from mixtures of magnetite and various promoters using the facilities of the Ceramics Program of the Materials Research Laboratory at SRI.

Substitution or supplementation of the sulfur-treated FTS catalysts will be expected during the project, possibly as a result of contact with other DOE contractors or upon the direction of the DOE project manager.

Characterization techniques, in addition to the characterization and reaction studies of Task 3, as described below, may be required to check the uniformity and degree of sulfur coverage of the sulfur-treated catalysts, especially those with very low sulfur coverage. Destructive temperature-programmed reduction of a sample of the treated catalyst to 1500 K with 100-kPa hydrogen will be used to verify the amount of chemisorbed sulfur and qualitatively determine its binding enthalpy. Also, the capacity of the sulfur-treated and reduced catalyst for additional sulfur adsorption (to saturation) at 373 K relative to the capacity of the fresh untreated catalyst is another way of determining the relative sulfur coverage<sup>22</sup> along with the more conventional chemisorption techniques of Task 3. Characterization studies for selected low-sulfur coverage catalysts will be conducted in an apparatus dedicated to temperature-programmed reaction experiments; this system uses on-line mass spectrometric and (for H<sub>2</sub>S) photoionization or flame-photometric gas analysis.

### Task 3: Characterization and Testing of FTS Catalysts

The goal of Task 3 is to characterize and determine the activity and selectivity of the catalysts prepared in both Tasks 1 and 2 relative to the standard base catalyst, a precipitated iron FTS catalyst. A schematic diagram of the microreactor system used to conduct the tests is shown in Figure 2. The catalysts will be reduced under typical reduction conditions and the specific metal surface area will be determined by dynamic BET adsorption with N<sub>2</sub>, or, if appropriate by CO and H<sub>2</sub> chemisorption at 325 and 300 K, respectively. The catalysts will then be used for FTS with 100-kPa synthesis gas of fixed composition (H<sub>2</sub>:CO = 2:1) in the fixed-bed isothermal microreactor. The FTS product distribution and syngas conversion will be determined for several reaction temperatures from 475 to 575 K. An automated two-column gas

chromatograph (Carle) will be used to follow the methane yield and the overall CO conversion rate. A second temperature-programmable gas chromatograph (Hewlett-Packard) with a flame ionization detector will be used to measure the product distribution for these tests up through at least carbon number C<sub>5</sub>. (For specification of the test parameters, see Table 2.) The gas flow rate and catalyst bed will be adjusted to keep the initial CO conversion near 20%.

Key test results will be the methane yield, the C<sub>5+</sub> hydrocarbon yield, and the CO conversion as a function of time over the 2-hour reaction period. These results will be used to give timely feedback about the success of the surface-confined cluster catalyst synthesis and the sulfur treatment of FTS catalysts; in this way we can modify the catalyst preparation methods of Tasks 1 and 2, and efficiently pursue the most promising catalyst formulations.

Promising catalysts, that is, those with methane yield significantly reduced over the base catalyst, or those with higher activity and good stability, will be subjected to more realistic FTS conditions in Task 4. Figure 3 is a flow chart of the decision analyses to be followed during synthesis and testing of the FTS catalysts.

In addition to surface area measurements and determination, FTS activity, and selectivity, the tests of Task 3 will include special temperature-programmed desorption experiments to provide information useful in the synthesis and activation of the multiatomic surface-confined cluster catalysts. The catalysts prepared under Task 1 will be stored in a nonactivated state in a dry box under reduced temperatures. These catalysts will be loaded into a sealed microreactor assembly, removed from the dry box, and placed in the characterization and FTS testing apparatus (Figure 2). The catalysts will be temperature-programmed from 300 K to perhaps as high as 800 K in helium or hydrogen carrier gas streams so as to determine the amount and temperature of propene, ethylene, and CO evolution as the original metal cluster-pendant group bonds are broken and the cluster interacts more completely with the support.<sup>6,7</sup> This information will be provided real-time by on-line mass