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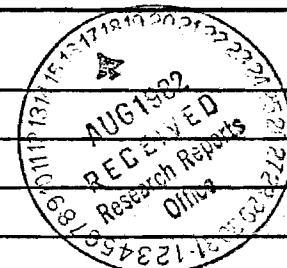
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"Bimetallic Supported Clusters in Fischer-Tropsch Synthesis"

Annual Progress Report (Covering the Period  
September 1, 1982 to August 31, 1983)

submitted to

Engineering Foundation  
United Engineering Center  
345 East 47th Street  
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by

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## INTRODUCTION

It appears likely that the initial application of Fischer-Tropsch synthesis would be in the production of specialty chemicals and petrochemical feedstocks. This has renewed much interest in the product distribution during Fischer-Tropsch reactions and in the identification of reaction intermediates during the chain-growth process as evident from the two recent reviews in this area (1, 2). It is obvious that an improved understanding of the chain-growth steps and the intermediates involved therein might lead to the development of more selective catalysts. Several studies (3-7) suggest that the chain-growth in F-T synthesis is a process analogous to a conventional polymerization scheme in which the chain growth occurs via the insertion of a monomer to a growing polymer chain and thus the product distribution during F-T synthesis might be described by the Schultz-Flory equation. In those instances where such a simplistic model does not fit the data, the role of secondary reactions such as readsorption or the involvement of chain units other than monomer has been envisaged; few attempts have been made to develop mathematical models which account for these secondary reactions in describing the product distribution (8, 9).

Yet, another approach has focused along the path of developing bimetallic catalysts to improve selectivity during CO hydrogenation. Undoubtedly, much impetus for this approach has been derived from the successful application of multimetallic catalysts in the petrochemical processes. A number of recent studies (10-12) have investigated bimetallic catalysts for CO hydrogenation. However, when both metals are known to be active in CO hydrogenation, changes in the activity and especially selectivity are difficult to interpret. For example, whether such changes are caused by alloying or by dilution of the

matrix of one metal with another metal, is not clear. Also the role of individual metal in the chain-growth process is not easily understood. On the other hand, if one chooses a combination of two metals such that only one of the two metals is active for the reaction then the results can be interpreted more easily. Still sufficient ambiguity remains in interpreting the results in terms of geometric vs. electronic effects. Also, the changes in selectivity are defined in terms of structure-sensitive and structure-insensitive reactions. The general scheme of reactions in F-T synthesis can be grouped in one of the two categories: (1) hydrogenation reaction and (2) polymerization reactions. Typical hydrogenation reactions are classified as facile or structure-insensitive reactions (13). However, the nature of polymerization reactions in the same context has not been defined. It has been reported that a minimum metal crystallite size is needed to form a hydrocarbon of certain chain length (4,6,14,15). Whether this crystallite size represents the minimum number of metal atoms (ensemble size) to catalyze the chain-growth process or whether the electronic structure (and hence catalytic properties) are modified has not been well understood. Our investigation was initiated with the above questions in mind. We have investigated the Ru-Cu/SiO<sub>2</sub> catalysts in CO hydrogenation reactions. Sinfelt and coworkers (16-18) have extensively studied this catalyst system in hydrogenation/hydrogenolysis reactions, and reported several orders of magnitude loss in the hydrogenolysis activity as compared to the hydrogenation activity. Few studies (12,19,20) have also been made to investigate this bimetallic catalyst system for the CO hydrogenation reaction. In one study (19), subatmospheric pressure conditions were used where CH<sub>4</sub> is the primary reaction product. Another study (12) employed atmospheric pressure conditions where only small quantities of C<sub>2</sub>-C<sub>4</sub> hydrocarbons were found. The only study in which significant quantities of higher hydrocarbons were formed

is by Nijs et al. (20). However, their results are difficult to interpret due to nonuniform distribution of the two metals on the zeolite support. Thus, the important aspects of product distribution changes remain unaddressed. Interestingly enough, our investigation may be interpreted either as an attempt to study the bimetallic catalysts using CO hydrogenation as a probe reaction, or it may be considered to be a study of the CO hydrogenation reactions by using bimetallic catalyst as a probe.

### OBJECTIVES AND SCOPE

The primary objective of our study was to investigate the nature of geometric vs. electronic effects in Ru-Cu catalysts and to study their effect (if any) on the activity and selectivity in the Fischer-Tropsch reaction. Such an understanding would undoubtedly be a useful guide in the development of more selective catalysts. The Ru-Cu bimetallic combination was chosen because of the immiscibility of Cu in Ru so that some insights into the ensemble size effects induced by the presence of Cu on Ru crystallite surface can be gained by using low-dispersed catalysts. At the same time, interactions of an electronic nature between Ru and Cu have been reported in the literature dealing with highly dispersed Ru-Cu catalysts. Thus, studies with low-dispersion and high-dispersion Ru-Cu catalysts are expected to provide an improved understanding of the geometric and electronic effects in bimetallic catalytic systems. The questions which our study has focused to address are:

- (1) How are the Ru surface area, dispersion and its reducibility influenced by the presence of Cu?
- (2) How does the presence of Cu effect the adsorption characteristics of individual reactant species?

- (3) What is the role of Ru-Cu interaction (at both, low and high dispersions) on the activity and selectivity in Fischer-Tropsch synthesis, and whether this catalytic behavior can be correlated with the adsorption properties of the active sites, dispersion, catalyst reducibility, etc.

#### SUMMARY OF WORK TO DATE

We initiated the experimental work on this project in June, 1982, and a summary of the results obtained during the past 15 months is described here. One graduate student, Mr. Billy Huh, has been working on this project and was responsible for setting up the reactor, flow system and analytical equipment. Mr. Huh finished his M.Ch.E. thesis work in December, 1982 and is continuing to work on the same project towards a Ph.D. degree.

Bimetallic Ru-Cu/SiO<sub>2</sub> catalysts have been prepared using coimpregnation and coreduction method; the loadings of both Ru and Cu were varied. Initial work was done using nonporous fumed silica (Cabosil HS5, Cabot Corporation) support to minimize the extent of transport effects which can be significant for the CO hydrogenation reaction. However, certain trends were observed, and we also included porous silica in our investigation to define the cause of these trends. The catalysts were characterized using x-ray line broadening, H<sub>2</sub> chemisorption, temperature-programmed desorption of CO, and transmission electron microscopy. The activity and selectivity behavior of these catalysts was studied in a shallow, fixed-bed reactor under differential-mode operation at temperatures between 473K and 573K and at two different pressures (100 kpa and 1000 kpa).

On poorly-dispersed Ru catalysts, the effect of Cu is one of blocking the surface sites active in CO hydrogenation. The methanation turnover numbers and the activation energy for methanation, however, remain virtually unaffected by the presence of Cu. The product distribution is shifted towards lower hydrocarbons in the presence of Cu, but a clear distinction between the C<sub>2</sub>-C<sub>4</sub> hydrocarbons and C<sub>5</sub><sup>+</sup> hydrocarbons can be made from our studies. The selectivity towards the formation of C<sub>2</sub>-C<sub>4</sub> hydrocarbons relative to methane is independent of the loadings of both metals, whereas the selectivity for the formation of C<sub>5</sub><sup>+</sup> hydrocarbons is reduced by several orders of magnitude upon the addition of Cu.

A careful analysis of the experimental data shows that the formation of higher hydrocarbons is not restricted by a reduction in the ensemble size of Ru. Rather, the fractional CO conversion (within the range of differential conversions) is a critical parameter in the formation of C<sub>5</sub><sup>+</sup> hydrocarbons, suggesting an important role of readsorption or other secondary processes in the synthesis of higher hydrocarbons. Our work with porous silica supported Ru catalysts confirms this trend. It appears that the observations made in the literature, which suggest the correlation between the crystallite size and the hydrocarbon chain length, may be due to the limitations of pore size itself imposed on the growth of hydrocarbon chain. We are presently attempting to prepare highly-dispersed Ru-Cu catalysts (with partial success so far) which will be studied to see the role of electronic interactions.

## EXPERIMENTAL

### (A) Apparatus

A diagram of the experimental flow system designed and built for this study is illustrated in Figure 1. Gases required were: ultra high purity

helium (Linde); oxygen (10% oxygen, balance helium, custom grade); ultra high purity hydrogen (Linde); carbon monoxide-hydrogen mixture (25% CO, 75% H<sub>2</sub>, primary grade, Linde) and 1% each of C<sub>1</sub> - C<sub>5</sub> in He primary standard mixture (Linde). All flow lines were 316 stainless steel tubings (6.35 or 3.175 mm OD).

Each of the gas cylinder lines was equipped with molecular sieve (Davison, Grade 521) trap (12.7 mm OD, 305 mm length stainless steel) mainly to remove moisture. Deoxo purifier (Englehard model D 10-2500 psia) was placed in hydrogen line and activated coconut charcoal (6-14 mesh, Fisher Scientific) was installed in CO/H<sub>2</sub> line. The purpose of these traps was to remove oxygen and carbonyl compounds respectively. As shown in the Figure 1, the combination of three-way valves allows passage of desired gas streams to the reactor. In addition, with flow controllers (Brooks 8744) and rotameters (Union Carbide) in the H<sub>2</sub> and CO/H<sub>2</sub> lines, the system was capable of changing the ratio of CO/H<sub>2</sub>.

Once the chosen gas stream reaches the by-pass point as shown in the diagram, it can either be sent to GC for an analysis or sent to the reactor. The stream sent to the reactor initially passes through a relief valve and flows downward through the catalyst bed. By connecting 4-way and 3-way valves together prior to the GC inlet, either the reactant/standard mixture or the product stream can be sent into the GC for an analysis, while the other line is being vented. In order to prevent the flow of gases being vented from returning to GC, another relief valve (Nupro, SS-2C-1) was installed next to the 4-way valve. For the measurement of high and low flow rates, a rotameter and a bubble flow meter were used respectively. From the combination of relief valve (Nupro, SS-2C-1) placed at the inlet and backpressure regulator (Tescom

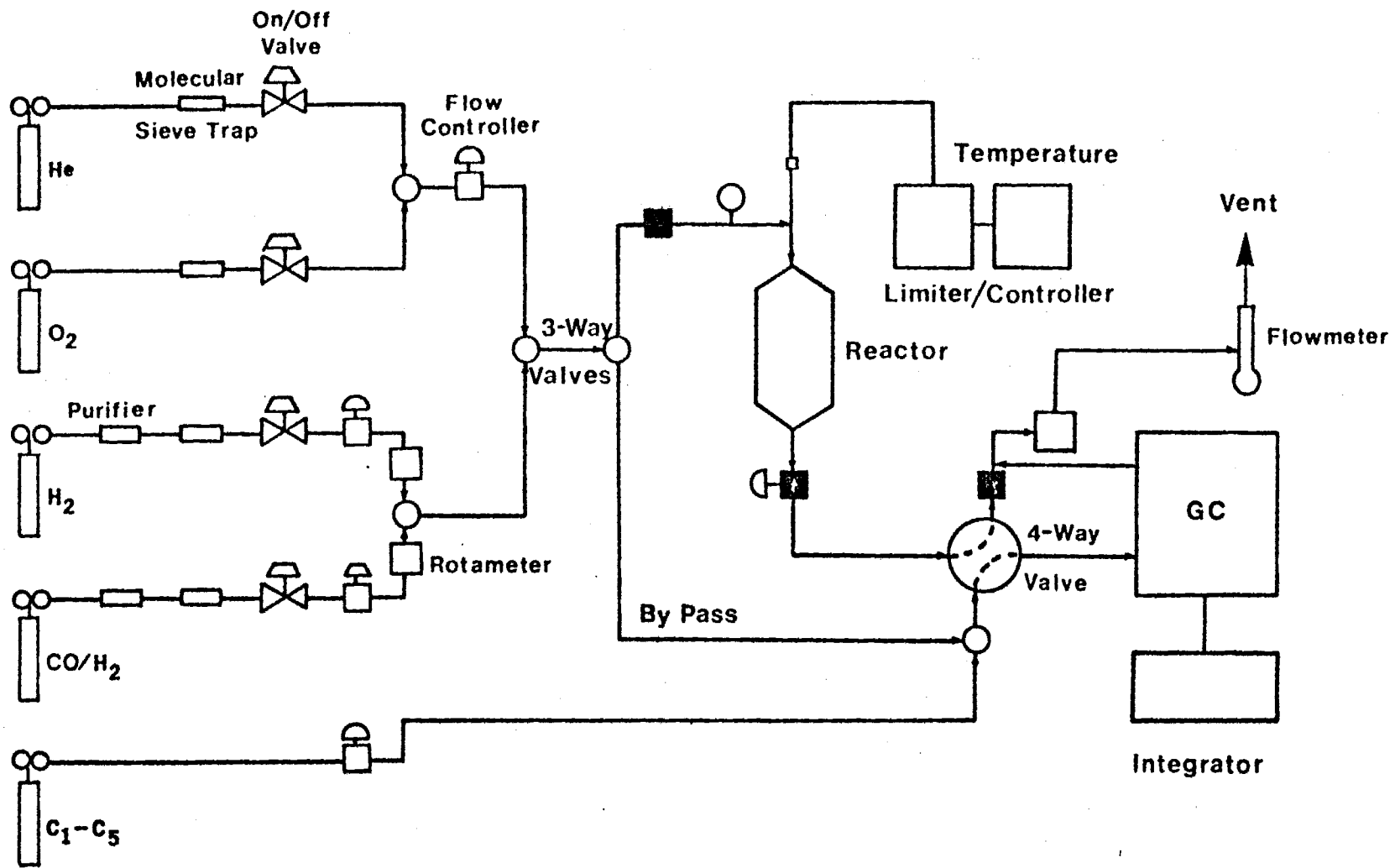


Figure 1. A Schematic Flow Diagram of Reactor Setup

model 44-2300) at the outlet of the reactor could be operated accurately at pressures between 1 and 20 atmosphere.

A plug-flow differential reactor made of stainless steel tube (1.27 cm OD, 61 cm long) was employed (Figure 2). The reactor was placed vertically inside the heating furnace (Lindberg, model 54032). The annular region between the reactor tube and heating coils of furnace was fitted with a copper tube (10 mm thickness) to provide a stable and uniform temperature in the catalyst bed. Typically 0.25 to 0.5 g of catalysts were charged in the center of the reactor supported between two glass wool plugs. Two thermocouples, one inside the catalyst bed and another in the annular region between the reactor and furnace, were employed. The former one was simply connected to a digital temperature readout (Omega 2166A), while the latter relayed the temperature to the Honeywell AV72 dialapak controller which supplied power to the furnace. In conjunction with the temperature controller, an Omega (model 50) on/off temperature limiter was used for safety reasons. The temperature of catalyst bed could be controlled up to 1100<sup>o</sup>K within an accuracy of 1<sup>o</sup>K.

#### (B) Analytical

The reactor effluent was analyzed by using an on-line gas chromatograph (Hewlet Packard 5710A) equipped with a flame ionization detector. From the effluent side of the reactor to the inlet of the GC, all the lines were wrapped with heating tape and insulated to prevent the condensation of higher hydrocarbons going into the GC. The on-line sampling 6-port valve was also kept at a high temperature (150<sup>o</sup>C) with a heating plate. Volume of sampling loop was 1 ml.

As a column packing, neutral alumina (certified grade, 80-200 mesh, Fisher-Scientific) was used to separate hydrocarbon products. Two identical

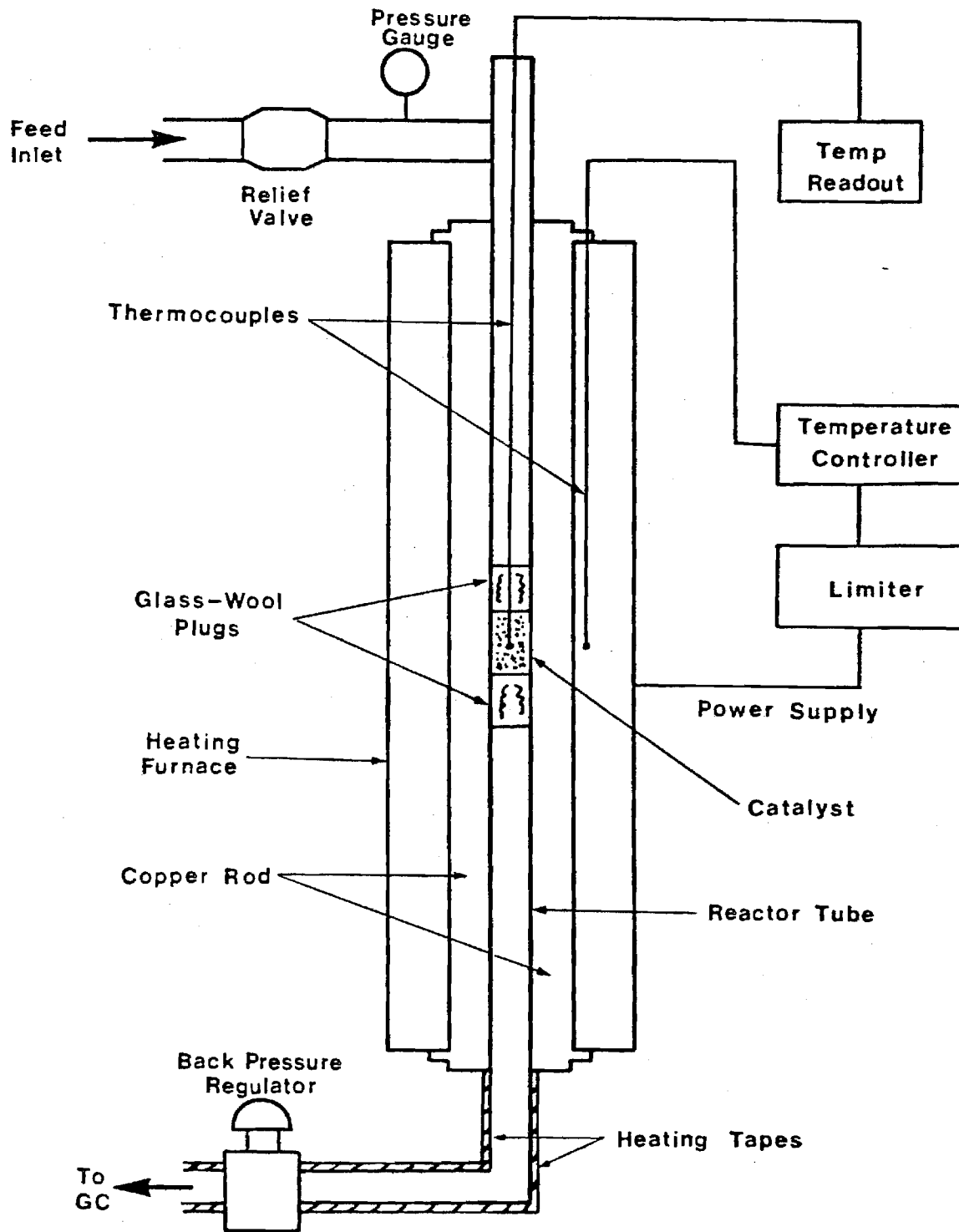


Figure 2. Reactor-Furnace Assembly

columns (6.35 mm dia, 1.83 m long) were used to circumvent the base line drift due to the temperature programming.

The flow rate of carrier gas, helium, was set at 40 cc/min, and that of hydrogen and air were 60 and 240 cc/min, respectively. The dual electrometer was set at differential mode and detector, sampling valve, and injection port temperatures were set at 300, 150, and 200°C, respectively. With oven temperature programming [50°C (2 min) to 280°C at a rate of 32°C/min and holding it at 280°C] C<sub>1</sub> to C<sub>10</sub> hydrocarbons were separated very well over a period of 28 minutes; the maximum sensitivity for the detector was about 1 ppm.

### (C) Experimental Procedure

Approximately, 0.25 to 0.50 g (typically 0.25 g) of catalysts were loaded into the reactor between the glass wool plugs, and a thermocouple was placed in the center of the catalyst bed. The reactor was secured with the furnace using Swagelok<sup>®</sup> fittings and reduced under flowing hydrogen (100 cc/min) for 3 hrs at 773°K. The reactor was then cooled to the desired reaction temperature (473 to 573°K) under flowing hydrogen. The flow stream was then switched to CO/H<sub>2</sub> mixture and the reactor was bypassed to measure impurities (usually methane) present in the CO/H<sub>2</sub> mixture. Periodically the reactants were also sent to another GC equipped with thermal conductivity (TC) detector cell (HP 5730A) to measure the CO concentration and to insure the absence of other impurities. After the reactant flow stream was switched to the reactor, back-pressure regulator was closed to build up pressure inside the reactor, and 4-way valve was positioned such that products were directed into the GC. When the pressure had reached 150 psia (or the desired operating pressure), back-pressure regulator was opened slightly to allow gases to flow, and the desired flow rate was set using the flow controller for CO/H<sub>2</sub> line. For this work, the CO/H<sub>2</sub> ratio was kept constant at 1:3. The samples were injected into

GC every 30 min. for analysis, and flow-rate was checked between each sampling. The kinetic measurements were made when a steady state activity was reached. The operating variables for the kinetic study were flow rate, temperature, and pressure.

#### (D) Catalyst Characterization

The main objectives of catalyst characterization were to obtain crystallite size and Ru metal surface area. The average crystallite size of the catalysts was measured using the line broadening method of X-ray diffraction.

Since amorphous silica was used as support, no background peaks due to the carrier were detectable. Ruthenium has a major diffraction peak (100) at 38.4 ( $2\theta$ ) degrees. There were no visible lines due to copper in the scan of the Ru-Cu catalyst indicating the absence of copper crystallites larger than 50 Å. In this work, a sintered MgO was used to obtain instrumental line broadening.

Temperature-programmed desorption (TPD) was also used to characterize catalysts. Helium gas was used as the carrier, and liquid nitrogen trap was placed on the helium line to remove moisture and oxygen. Dry ice-acetone trap ( $-75^{\circ}\text{C}$ ) was placed on the effluent side of the reactor to remove carbon dioxide formed by CO disproportionation, if any, during the desorption process. Even though Ru was supported on high surface area silica ( $300\text{ m}^2/\text{g}$ ), it was necessary to increase sample loadings from 50 mg to 100 mg as the catalysts containing increasing amounts of Cu were studied; this was done in order to detect the signal of the CO desorbed from the catalyst into the helium gas stream.

The ruthenium surface area was measured using hydrogen chemisorption. The chemisorption apparatus consisted of an Edwards's Cryo-cooled Diffstak-63

oil diffusion pump, an EDM2 mechanical pump, and two MKS Baratron 200A pressure gauges with ranges from 0 to 100 and 0 to 1000 Torr. The adsorption cell was made of quartz, and it was connected to the system with Cajon Ultratorr fittings. Hydrogen and helium (both ultra high purity, Linde) were both passed through liquid nitrogen trap to remove any  $O_2$  or  $H_2O$  traces.

Transmission Electron Microscopy (TEM) was also used for catalyst characterization. Approximately  $1 \text{ mm}^3$  of reduced powdered sample was placed in the bottom of a polyethylene capsule which was filled with resin (methyl methacrylate with 2 wt% benzoyl peroxide as curing agent). After gently stirring the sample, it was allowed to polymerize overnight at  $320^\circ\text{K}$ . The solidified resin block was then trimmed and pre-cut in a Reichert OM-U2 ultramicrotome with a glass knife to produce a smooth surface. Then the sections were cut in the same ultramicrotome using a diamond knife and mounted on carbon coated TEM grids. The scanning was done on a Phillips EM-200 electron microscope at 200 KV using Kodak 5302 35 mm film, and the magnification was 118,580 X for all the micrographs.

#### (E) Catalyst Preparation

At the beginning in our work, all the catalysts were prepared by using aqueous impregnation method which resulted in poorly dispersed Ru catalysts. Subsequently other techniques were also tried which are briefly summarized below.

##### (i) Aqueous Impregnation

The catalysts were prepared by coimpregnation procedure, using aqueous solutions of ruthenium trichloride (43.53% Ru, Alfa Products) and copper (II) nitrate (26.3% Cu, Alfa Products). The support was an amorphous fumed silica known as Cabosil HS5 (Cabot Corporation, Boston, Massachusetts) and had a BET surface area of  $300 \text{ m}^2/\text{g}$ . In order to prepare 8% Ru-1.257% Cu

supported on  $\text{SiO}_2$ , a mixture of 32 ml of 1% Ru solution and 5 ml of 1% Cu solution was slowly added to the 3.6297 g of silica, while stirring with magnetic stirrer. The silica had been wetted with deionized water prior to adding metal solutions to ensure uniform mixing. After the impregnation, the resulting slurry was transferred to an oven and dried in air for 14 hrs at  $388^\circ\text{K}$ . The dried catalyst was then crushed finely and stored in sample vials. The catalysts consisting of just one metal (Ru) were prepared in the same manner as the bimetallic catalysts, except that the impregnating solution contained only one metal salt.

#### (ii) Aqueous Coreduction

The basis of this technique is that when the pH of the solution containing both  $\text{RuCl}_3$  and  $\text{SiO}_2$  is increased at slow rate, precipitated ruthenium may adsorb on the silica support giving uniform distribution. An attempt was made to slowly precipitate ruthenium from the aqueous chloro-anion solution onto the silica support by slowly adding hydrazine hydrate.

An appropriate amount of  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$  (43.53% Ru) was dissolved in the excess water (20 cc/gm of  $\text{SiO}_2$ ) followed by slowly adding the calculated amount of  $\text{SiO}_2$  while stirring with magnetic stir. Once the solution is well mixed, diluted hydrazine hydrate solution (20% by volume in  $\text{H}_2\text{O}$ ) was added dropwise (5 min interval between the drop) with continuous stirring until the pH of mixture has reached 9.3. When the evolution of  $\text{N}_2$  had subsided to a low level, the solution was allowed to stand overnight at room temperature with occasional shaking. This mixture was then filtered, and catalyst was washed with cold 2M ammonia. The filtrate and washings were analyzed for Ru content by atomic absorption spectroscopy to obtain a value for the amount of Ru incorporated in the catalyst. The resulting catalyst was air dried at  $120^\circ\text{C}$  for three hrs. and was crushed and sieved (200 mesh) before characterizing it.

(iii) Non-aqueous Impregnation

It has been suggested that the difficulty of preparing highly-dispersed Ru catalysts is related to the hydrolysis of the support by the aqueous (protic) solvent. By using aprotic solvents, such as acetone or acetonitrile, the hydrolysis reactions with hydroxyl groups (silanol) are minimized, allowing selective adsorption of  $\text{RuCl}_3$  onto the support.

The impregnation of Ru onto the  $\text{SiO}_2$  using aprotic solvents (acetone, acetonitrile) was done as follows. A known amount of  $\text{RuCl}_3$  salt was first dissolved into the solvent (20 cc of solvent/gm  $\text{SiO}_2$ ). Once the salt is completely dissolved, silica was added slowly while stirring with a magnetic stir. The mixture was continuously stirred until all the solvent has been evaporated at room temperature (3 to 4 hrs). The resulting catalyst was air dried at  $120^\circ\text{C}$  for 3 hr prior to the reduction stage. The dehydration of the  $\text{SiO}_2$  support was carried out overnight at  $500^\circ\text{C}$  in flowing helium, and all resulting catalysts were again firmly crushed and sieved before hydrogen chemisorption.

## RESULTS AND DISCUSSION

(a) Catalyst Preparation and Characterization

Table I lists the composition of catalysts prepared by the aqueous impregnation procedure. Some of these catalysts were characterized by using  $H_2$  chemisorption, x-ray line broadening, and transmission electron microscopy; the results are summarized in Table II. There is a fair degree of agreement between the results obtained from  $H_2$  chemisorption, TEM, and x-ray line broadening measurements; the mean Ru crystallite size appears to be around  $15 \pm 5$  nm. Although the catalyst support and the impregnating solution used to prepare catalysts in our study were similar to those used by Sinfelt (16), we were unsuccessful in obtaining highly dispersed Ru/SiO<sub>2</sub> catalysts as was claimed in the study by Sinfelt. It has been suggested that the aqueous impregnation technique leads to very poorly dispersed Ru catalysts and aprotic solvents such as acetone may be used to obtain well-dispersed Ru catalysts (21). It is also noteworthy that the Ru crystallite size appears to be independent of the metal loading (over a range of one to eight weight percent), further supporting the fact that the poor degree of dispersion is a result of the preparation technique itself.

For Ru-Cu catalysts, x-ray line broadening studies indicated that the Ru crystallite had not changed to any noticeable extent from what it was in the absence of Cu. Thus a decrease in the Ru surface area (as measured by  $H_2$  chemisorption) may be interpreted as due to the blocking of Ru surface atoms by copper atoms. However, Ru and Cu are immiscible metals and in order to minimize the surface free energy of the mixture, the Cu atoms will be preferentially segregated to the surface of Ru crystallites. The above model is supported by an EXAFS (extended x-ray absorption fine structure)

Table I

Composition\* (weight percent) of CatalystsPrepared by Aqueous Impregnation Method

<u>Sample</u>	<u>% Ru</u>	<u>% Cu</u>	<u>Atomic Ratio Cu/Ru</u>
A	1	0	0
B	5	0	0
C1	8	0	0
C2	8	1.26	0.25
C3	8	2.51	0.50
C4	8	5.02	1.00
D	0	5.02	

\* balance silica

Table II  
Average Crystallite Size Measurements  
from Various Techniques

Catalyst <sup>*</sup>	H <sub>2</sub> Chemisorption	X-ray Line Broadening	Transmission Electron Microscopy
A	235 A <sup>0</sup>	200 A <sup>0</sup>	---
C1	100 A <sup>0</sup>	200 A <sup>0</sup>	150 - 200 A <sup>0</sup>
C4	---	200 A <sup>0</sup>	---
D	---	230 A <sup>0</sup>	---

\* Refer to Table I

study which reported (18) that Ru in the bimetallic clusters appeared to be very similar to the Ru on a Cu-free SiO<sub>2</sub>-supported catalyst. The Ru atoms were coordinated mostly to other Ru atoms and only to a negligible extent to Cu atoms, whereas the coordination of the Cu atoms was believed to be evenly distributed between the Cu and the Ru atoms. Such a phenomenon will be especially true for the Ru metal crystallites whose surface is saturated by the Cu atoms. If we assume that one surface Ru atom is poisoned by one Cu atom in terms of its hydrogen chemisorption capacity, then an estimate can be made as to what amount of Cu might be needed to completely poison the Ru surface. For 8% Ru/SiO<sub>2</sub> catalyst (sample C1, Table I), the Ru metal surface area is found to be 4 m<sup>2</sup>/gm. It is estimated that the necessary Cu loading will be 0.63 weight percent to completely poison the available Ru surface. It is clear from Table I that sufficient Cu atoms are present even in the lowest loading Ru-Cu catalyst (sample C2) to completely block the H<sub>2</sub> chemisorption sites on the Ru surface. The results of Ertl and coworkers indicate a very dramatic effect of Cu on the hydrogen chemisorption capacity of Ru. They obtained chemisorption data on Ru (0001) single crystal surfaces, doped with submonolayer coverages of Cu and reported that with only 10% Cu overlayer, about 90% of the hydrogen chemisorption capacity had been lost (22). They obtained similar results with CO chemisorption studies also (22). Their results imply that one Cu atom may be able to poison about 8-10 surface Ru atoms in terms of hydrogen chemisorption capacity.

Whether these results obtained for Ru single crystal surfaces are applicable to supported Ru catalysts is not very well demonstrated, but it is clear that in our work, Cu was present in excess quantities and quite likely some of the Cu may have been present on the SiO<sub>2</sub> surface, especially for higher Cu loadings. The results of our work do not indicate as to what

fraction of Cu was present in association with the Ru crystallites and what fraction was present as "free" Cu on the SiO<sub>2</sub> surface. In any event, our failure to observe any Cu crystallite peaks by x-ray diffraction for the catalyst sample C4 (while we were able to observe a large Cu peak for sample D) indicates that the Cu associated with the Ru crystallites must have been much more than the amount dictated by the stoichiometry observed by Shimizu et al. (22) and perhaps even more than the 0.63 wt. percent Cu which we calculated on the basis of one Cu atom poisoning one Ru surface atom. It has been suggested that isolated Cu atoms are located in sites with highest coordination, i.e. the three-fold sites of the Ru (0001) surface (23). Quite likely such an idealized model may be applicable to the single crystal Ru (0001) surface resulting in the poisoning of more than one surface Ru atom by one Cu atom. For supported Ru catalysts, on the other hand, many different crystal surfaces may be present, including defect sites. Their susceptibility to poisoning by Cu is not known. Sinfelt (16) studied highly dispersed (D ~ 50%) Ru-Cu catalysts and reported only a ~ 40% drop in the hydrogen chemisorption capacity when the Cu/Ru atomic ratio was increased from zero to unity. Bond and Turnham (19) studied Ru-Cu catalysts in which the dispersion of Ru was estimated to be about 20-35%. They observed essentially no decrease in CO uptake as the Cu/Ru atomic ratio was increased from 0 to 1. In fact, in some cases an increase in the CO uptake was observed at intermediate loadings of Cu. It is possible that some of the Cu may have been present in the oxide form in their work, leading to increased CO chemisorption. Both these studies (16,19) indicate a very small effect of Cu on the hydrogen and carbon monoxide chemisorption capacity of Ru. In our work, the Ru crystallites are very large and the dispersion of Ru is about 4%. Thus, it is possible to observe a more dramatic decrease in the chemisorption capacity of Ru with only a slight amount of Cu.

The temperature-programmed desorption (TPD) spectrum for CO on Ru/SiO<sub>2</sub> shows two broad desorption peaks (Figure 3) -- one in the low temperature range (320<sup>o</sup>K to 550<sup>o</sup>K) which consists of four bands and the second in the range of 575<sup>o</sup>K - 775<sup>o</sup>K. Gonzalez and Miura (24) studied CO adsorption on Ru/SiO<sub>2</sub> catalysts using infrared spectroscopy and desorption of CO was investigated using TPD method. They reported a rather broad peak in the TPD spectra in the range of 300 K to 500 K with a peak maxima around 475 K. In consistency with their results from IR studies they suggested that this desorption peak was due to linearly adsorbed CO on Ru. A second peak in the TPD spectra was observed with maxima around 650 K which increased in intensity with the promotion of Ru catalyst with K<sub>2</sub>O. They suggested that the high temperature peak (lower IR frequency) was due to strongly bonded (perhaps bridge-bonded) CO. It was also reported (24) that higher temperature peak intensity increased with the pretreatment of catalyst with H<sub>2</sub>O prior to CO TPD experiment, and they speculated that it may have been due to the reaction between carbon and H<sub>2</sub>O arising from the dehydroxylation of the silica support. In previous studies (25,26), high temperature peak has been observed on alumina-supported as well as on silica-supported Ru catalysts. Furthermore, in a TPD study of CO desorption from Ru (0001) surface, a high temperature desorption state was observed (27). It thus appears likely that the specific Ru surface sites (high coordination) may be responsible for higher temperature CO desorption state to a much greater extent than the role played by hydroxyl groups on the support.

The Curve a in Figure 3 shows the TPD spectra of a Ru catalyst containing no copper. As copper is added to the Ru catalyst (Curve b), the low temperature peak position remains unchanged and the structure of four bands also remains preserved, only the intensity is drastically reduced.

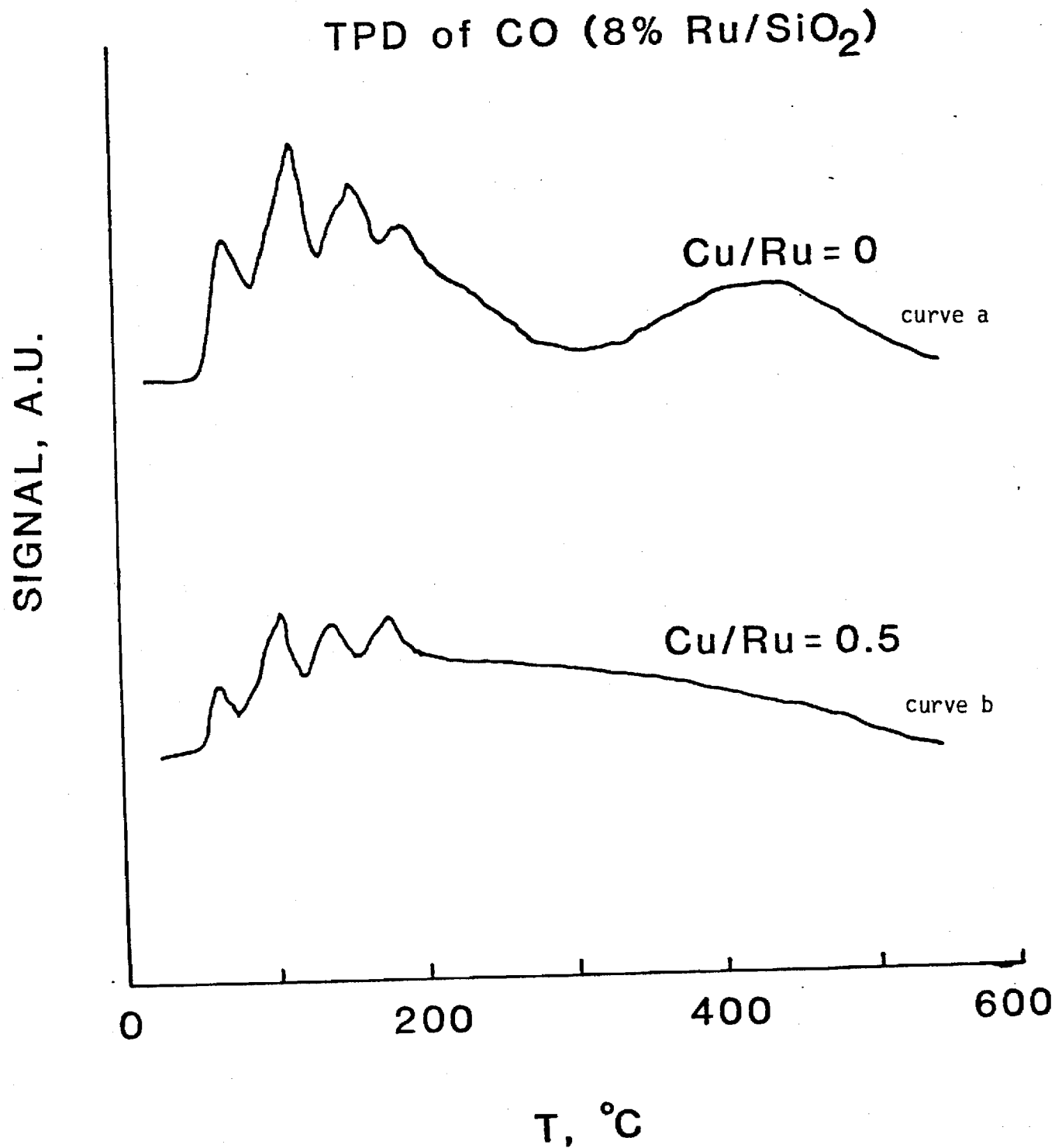


Figure 3. TPD Chromatograms over Ru/SiO<sub>2</sub>  
Heating Rate: 20°C/min.

However, a much more dramatic effect is observed for the high temperature peak; this peak intensity is almost completely diminished with the small quantities of copper. This observation is not surprising since the presence of Cu on the Ru surface, while reducing the total number of sites for CO adsorption, would preferentially eliminate the bridge-bonding CO sites. Thus the following statements can be made based on these TPD studies: (1) bridge-bonded CO adsorption sites are quickly eliminated in the presence of Cu, and the effect appears to be just a surface blockage (or geometric effect), and (2) while the intensity of linearly-bonded CO sites is reduced, the position of the broad peak and the band structure is preserved. This again indicates that the presence of Cu does not affect the strength of metal-carbon bond in the linearly bonded CO on the remainder of Ru surface sites.

In the results presented above, all the catalysts were prepared by aqueous impregnation method which resulted in a rather poor Ru dispersion. Under these conditions, the effect of Cu appears to be primarily geometric in nature i.e. of blocking the active Ru surface sites. Another series of catalysts of interest to us is highly-dispersed Ru/SiO<sub>2</sub> catalysts. Several studies show that the catalysts prepared by aqueous impregnation of SiO<sub>2</sub> with RuCl<sub>3</sub> solution give poor dispersion (14, 28-30). The higher dispersion of Ru on SiO<sub>2</sub> reported by Sinfelt and coworkers (16-18) has not been reproduced. The ion exchange method has shown to give highly dispersed catalysts on zeolite supports (12, 20); however, this technique has limited success with SiO<sub>2</sub> supports due to their lack of anion exchange capacity (31). Hence we attempted to prepare highly dispersed Ru/SiO<sub>2</sub> catalysts by using coreduction method and impregnation using nonaqueous solvents such as acetone and acetonitrile. Even the protic non-aqueous solvents e.g. methanol and

ethanol can interact strongly with the dehydrated silica surface by hydrogen bond to form charged polar layers to inhibit uniform adsorption of the Ru salt (32). Thus we limited ourselves to using aprotic solvents like acetone and acetonitrile. Table III lists the catalysts prepared by these alternate methods and their mean Ru particle size, characterized by  $H_2$  chemisorption experiments. We would like to note here that this is our latest work in order to prepare highly dispersed Ru catalysts and we have not conducted any reaction studies.

As shown in Table III, the coreduction method using hydrazine resulted in about a 2-fold increase in the Ru metal dispersion as compared to that using aqueous impregnation. However, the dispersion of  $\sim 8\%$  is still quite low. The use of aprotic solvents resulted in getting much better dispersion ( $\sim 15-20\%$ ). Various pretreatments of  $SiO_2$  support (dehydration and/or prewetting) and the drying method do not seem to have a significant effect on the degree of dispersion.

The surface of silica support is fairly heteronegeous with presence of different sites. One of them is siloxane, which is formed by bridge bond formation of oxygen with two silicon atoms. On the other hand, in ambient temperature the majority of the surface oxygen is in the hydroxylated form called silanol. These silanols are capable of existing as an isolated hydroxyl group surrounded by the siloxane group or form hydrogen bonds with other silanols when in proximity. Both isolated and hydrogen bonded surface hydroxyl groups are polar and extremely hydrophillic in nature, while siloxane groups are nonpolar and hydrophobic in nature. It is possible that trace quantities of water are present in the aprotic solvents so that the dehydrated silica surface readily forms hydroxyl groups. In future efforts, an attempt will be made to remove any water impurity from these aprotic solvents.

Table III

Catalyst Characterization (prepared by different methods) by H<sub>2</sub> Chemisorption

<u>Catalyst</u>	<u>Method of Prep</u>	<u>Solvent</u>	<u>% Ru</u>	<u>% D</u>	<u>d, A<sup>0</sup></u>	<u>Silica Pretreatment</u>		<u>Catalyst Drying</u>
						dehydration	prewetting	
A	Aqueous Impreg.	H <sub>2</sub> O	1	4.6%	200	No	No	120°C in air
B	Coreduction with hydrazine	H <sub>2</sub> O	1	7.9%	130	No	Yes	-- do --
C	Nonaqueous Impreg.	Acetone	1	16%	67	No	No	-- do --
D	-- do --	Acetone	1	16%	67	Yes	Yes	Vacuum (50°C)
E	-- do --	Acetonitrile	1	20%	54	Yes	Yes	-- do --
F	-- do --	-- do --	0.5	13%	80	Yes	Yes	No
G	-- do --	-- do --	0.5	18.4%	59	Yes	Yes	Vacuum (50°C)

(b) Reaction Studies

Most of the reaction studies have been conducted using the catalysts prepared by aqueous impregnation procedure (Table I). Some work has also been done using Ru catalysts supported on porous silica and we will briefly summarize those results. The focus below should be on the catalysts shown in Table I.

(i) Activity and Activation Energy for Methanation

Table IV summarizes the methanation turnover numbers and the activation energy for methanation over 8% Ru/SiO<sub>2</sub> catalysts at 523°K and at 1000 kpa. These turnover numbers were calculated on the basis of H<sub>2</sub> chemisorption data. It is evident that the methanation turnover numbers are independent of the Cu/Ru ratio. Also, the activation energy for methanation appears to be more or less insensitive to the presence of Cu; the activation energy measurements were made over a temperature range of 475 K - 600 K.

Additional evidence for the role of Cu in Ru/SiO<sub>2</sub> as a purely geometric effect comes from the reaction studies. The Table IV clearly shows that while the Ru surface area decreases by more than an order of magnitude by the presence of Cu, the methanation turnover numbers remain constant within a factor of two over the entire range of Cu loadings. The hydrogenation reactions are considered to be facile in nature (13), i.e., the rate is not influenced by the structure or the ensemble size other than a decrease corresponding to the total Ru metal surface area. Table IV indicates that the activation energy for methane formation undergoes a small increase from  $20 \pm 3$  Kcal/mole to  $24 \pm 3$  Kcal/mole as the Cu/Ru atomic ratio increases from 0 to 1. Because of the possibility of large error in the measurements of activation energy, we cannot be sure whether this apparent

Table IV

Steady State Methanation Activity of Ru-CuCatalysts at 523<sup>0</sup>K, 10 atm

<u>Catalyst</u>	<u>N<sub>CH<sub>4</sub></sub></u>	<u>Ea<sub>CH<sub>4</sub></sub></u>
C1	0.32	20 ± 3
C2	0.66	21 ± 3
C3	0.47	23 ± 3
C4	0.38	24 ± 3

increase in the activation energy is real. Bond and Turnham (19) studied CO hydrogenation over Ru-Cu/SiO<sub>2</sub> catalysts at subatmospheric pressure reaction conditions and reported a constant activation energy of  $21 \pm 2$  Kcal/mole for methane formation, which is in excellent agreement with our experimental results. However, they reported a 50-fold decrease in the methanation turnover numbers as the Cu/Ru atomic ratio was increased from zero to unity. This is rather surprising since they observed no decrease in the CO chemisorption capacity of Ru/SiO<sub>2</sub> as more and more amounts of Cu were added to it. In addition, they observed that the methanation reaction was positive order with respect to the H<sub>2</sub> partial pressure and this order remained essentially unchanged as the atomic ratio of Cu/Ru was increased. However, they reported that the reaction dependence on the CO partial pressure changed from negative to positive order with the addition of Cu. If the reaction mechanism and the rate-controlling step remain unchanged with Cu addition, as was suggested by Bond and Turnham (19), one would expect the reaction dependence on CO partial pressure to change from negative to positive only if the equilibrium constant for the adsorption of CO on Ru is decreased in the presence of Cu. Apparently, this is in contrast with their observation that the CO adsorption capacity remained constant. We wish to speculate at this point that H<sub>2</sub> chemisorption rather than CO chemisorption capacity should be used to compute the turnover numbers. In a number of previous studies (5, 33), the multiple bonding of CO to smaller Ru crystallites has been observed; the same bonding is not observed for poorly dispersed catalysts. Thus it is possible that the true density of active sites is better represented by the H<sub>2</sub> chemisorption data.

Elliott and Lunsford (12) studied Ru-Cu bimetallics supported on Y-type zeolite; the Cu/Ru atomic ratio was varied between 0 and 6.5. It was found that the methanation turnover numbers decreased about 6-fold with an increasing

Cu content. The average Ru particle size in their study was in the range of 10-20 Å<sup>0</sup>. It is interesting, however, that they observed only a very small (by a factor of 2) decrease in the Ru surface area which was obtained from deuterium chemisorption data. Although the reasons are not obvious, we will like to note that in highly dispersed Ru-Cu catalysts (12,16,19), a very small decrease in the hydrogen or carbon monoxide chemisorption capacity is observed upon the addition of Cu, whereas in our low dispersion catalysts, a large decrease in the hydrogen chemisorption capacity is observed. Yet for these high-dispersion catalysts, significant decrease in the activity and the methanation turnover numbers is observed. Whether this decrease in the methanation turnover numbers is caused by the interaction between Ru and Cu or whether the role of Cu is a more indirect one, i.e., in increasing the Ru metal dispersion during the catalyst preparation steps is not clear. In one study (33), where the effect of the crystallite size of Ru supported on Al<sub>2</sub>O<sub>3</sub> was investigated, it was reported that the methanation turnover numbers decrease slowly with increasing dispersion of Ru at dispersion below 70%. However, for dispersion greater than 70%, very rapid decline in the specific methanation activity is observed as one increases the dispersion.

The reaction studies were made at two different pressures (100 kpa and 1000 kpa). Similar behavior was evident at both pressures. The major difference at higher pressure was increased selectivity towards the formation of higher hydrocarbons. Since, the product distribution was a major part of this study, the results below would emphasize those obtained at 1,000 kpa.

#### (ii) Product Distribution

Three loadings of Ru (1, 5, and 8 weight percent) were studied. Under identical operating conditions, an increase in the Ru loading caused an increase in the activity for CO hydrogenation on a per gram of catalyst

basis, as expected. More importantly, the selectivity for the formation of higher hydrocarbons increased. Figures 4 and 5 show the product distribution obtained for 1% Ru and 8% Ru respectively at 498<sup>o</sup>K and at 10 atm. For both catalysts, the primary product is methane, but the selectivity S increases almost by an order of magnitude as shown in Figure 6. The selectivity is defined as below

$$S = \frac{\text{amount of CO converted to } C_2 \text{ and higher hydrocarbons}}{\text{amount of CO converted to methane}} \quad (1)$$

The effect of Cu on the product distribution is shown in Figures 7 and 8 for two different loadings of Cu. A comparison with Figure 5 shows that the product distribution is altered significantly. While there appears to be little or no change in the formation of C<sub>2</sub>-C<sub>4</sub> hydrocarbons, substantial loss in selectivity for the C<sub>5</sub><sup>+</sup> hydrocarbons is evident. It appears quite interesting that the presence of Cu affected the formation of C<sub>2</sub>-C<sub>4</sub> hydrocarbons differently than that of C<sub>5</sub><sup>+</sup> hydrocarbons. Hence, the selectivity defined by eq. (1) was split in two parts:

$$S_{2-4} = \frac{\text{amount of CO converted to } C_2-C_4 \text{ hydrocarbons}}{\text{amount of CO converted to methane}} \quad (2)$$

and

$$S_5^+ = \frac{\text{amount of CO converted to } C_5^+ \text{ hydrocarbons}}{\text{amount of CO converted to methane}} \quad (3)$$

The data presented in Figures 5, 7, and 8 are plotted to represent the variation in selectivity (defined by equations 2 and 3) with the copper loadings, the results are shown in Figure 9 for 8% Ru catalysts at 498<sup>o</sup>K and at 10 atm. It is interesting that the selectivity S<sub>2-4</sub> remained independent of the Cu loading,

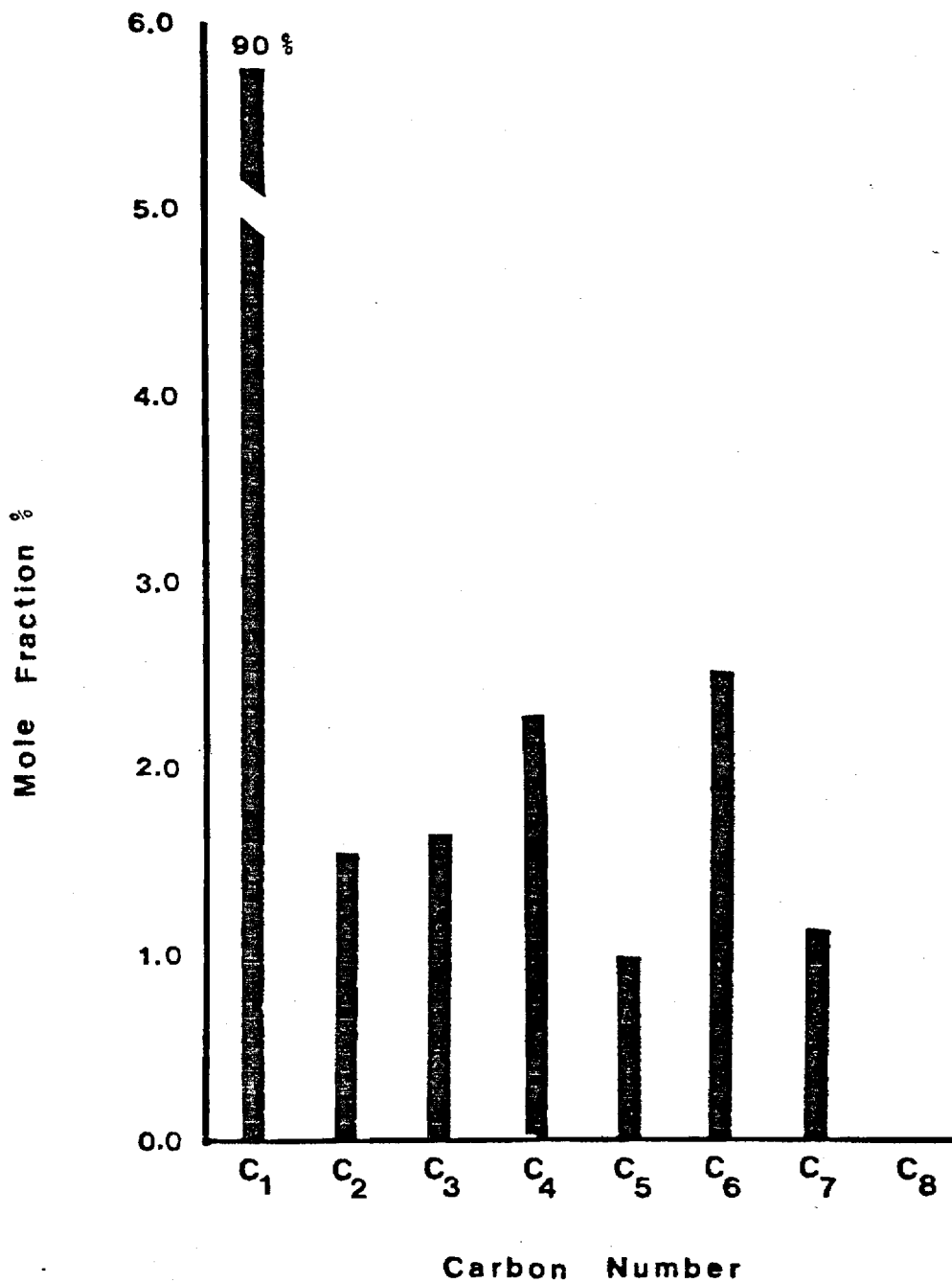


Figure 4. Product Distribution in CO Hydrogenation over 1% Ru/SiO<sub>2</sub> Catalyst at 498<sup>o</sup>K and at 10 atm.

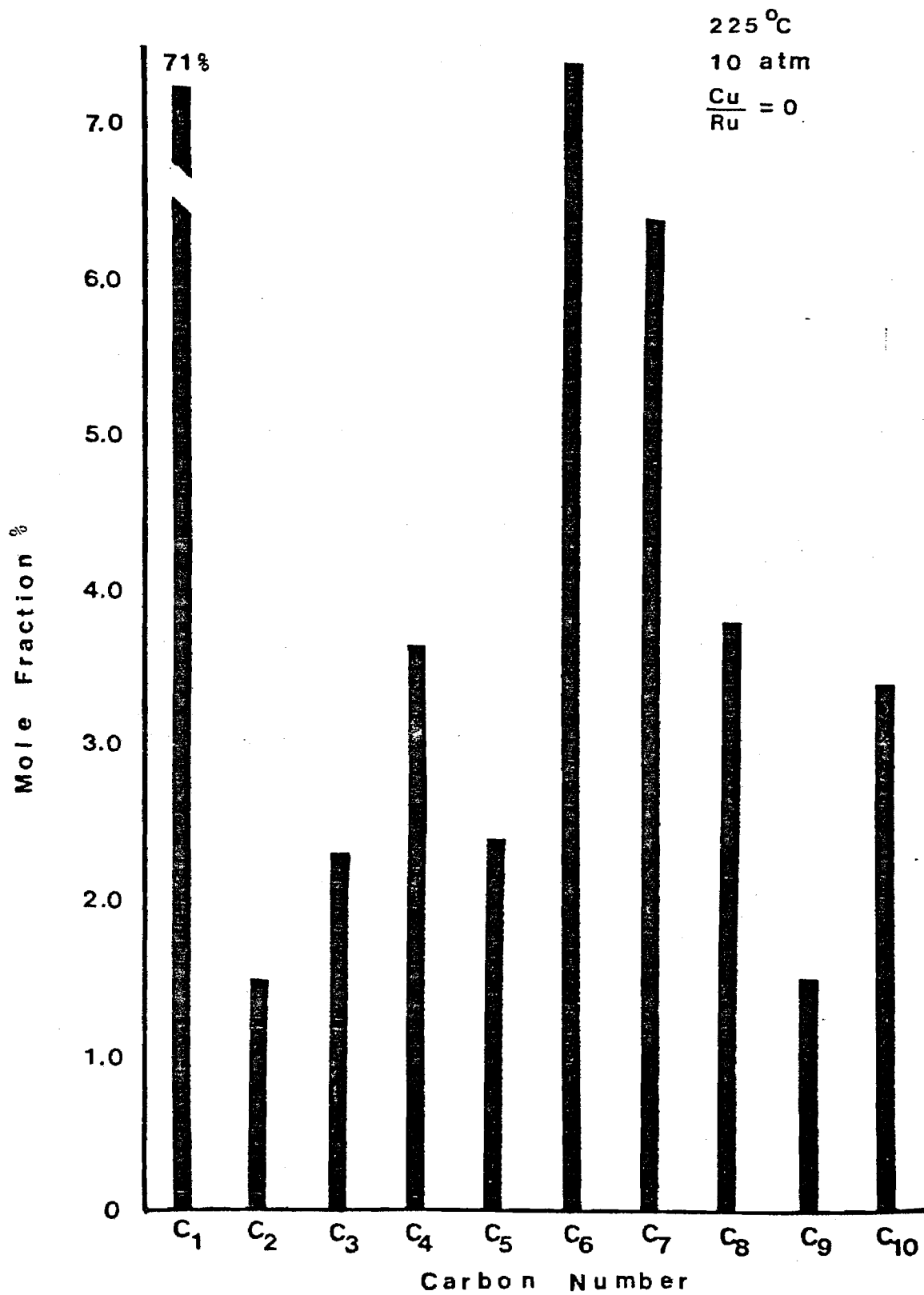


Figure 5: Product Distribution in CO Hydrogenation over 8% Ru/SiO<sub>2</sub> Catalyst at 498°K and at 10 atm.

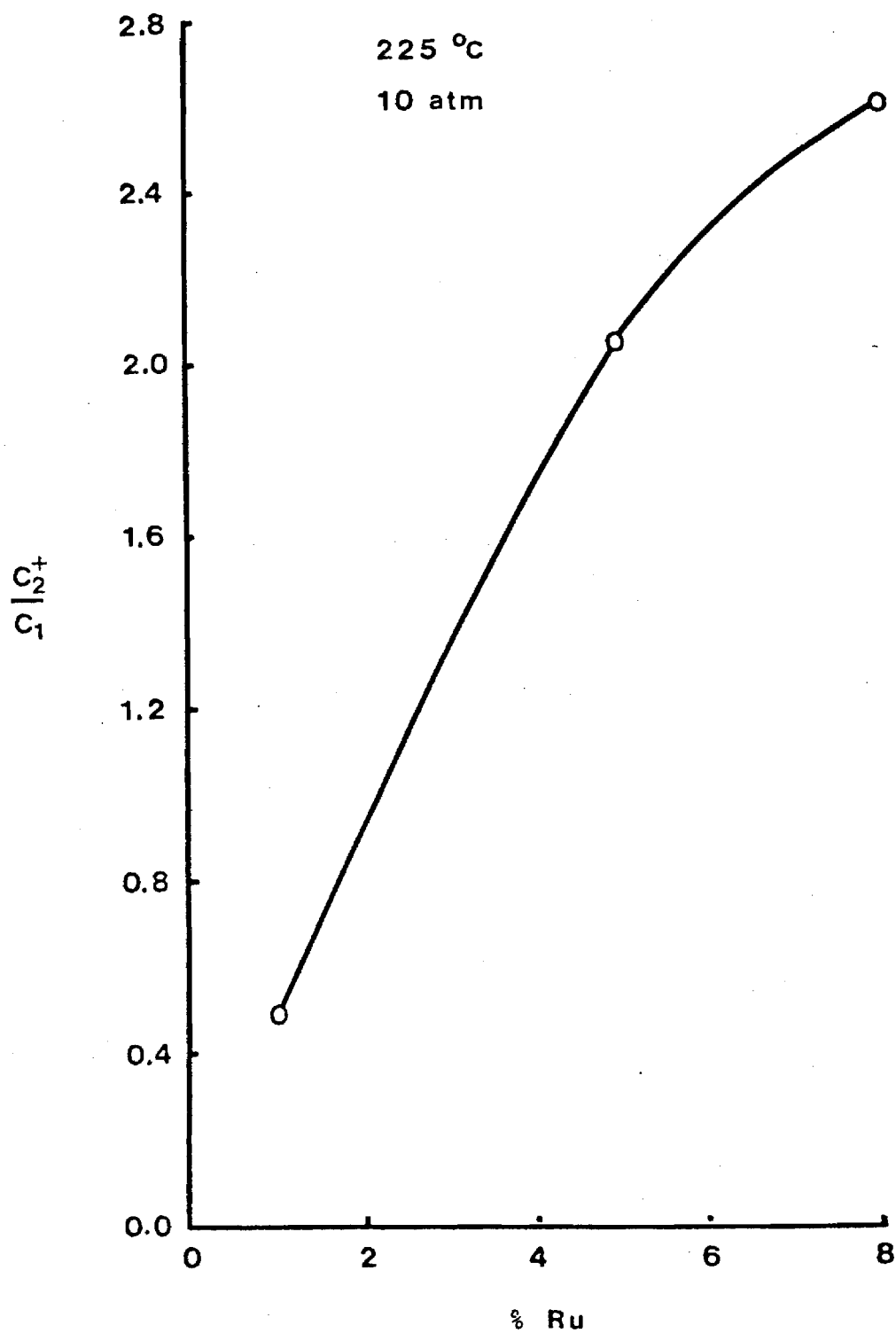


Figure 6. Selectivity for  $C_2$  and higher hydrocarbons with respect to methane on Cu-free Ru/SiO<sub>2</sub> Catalysts at 498°K and at 10 atm.

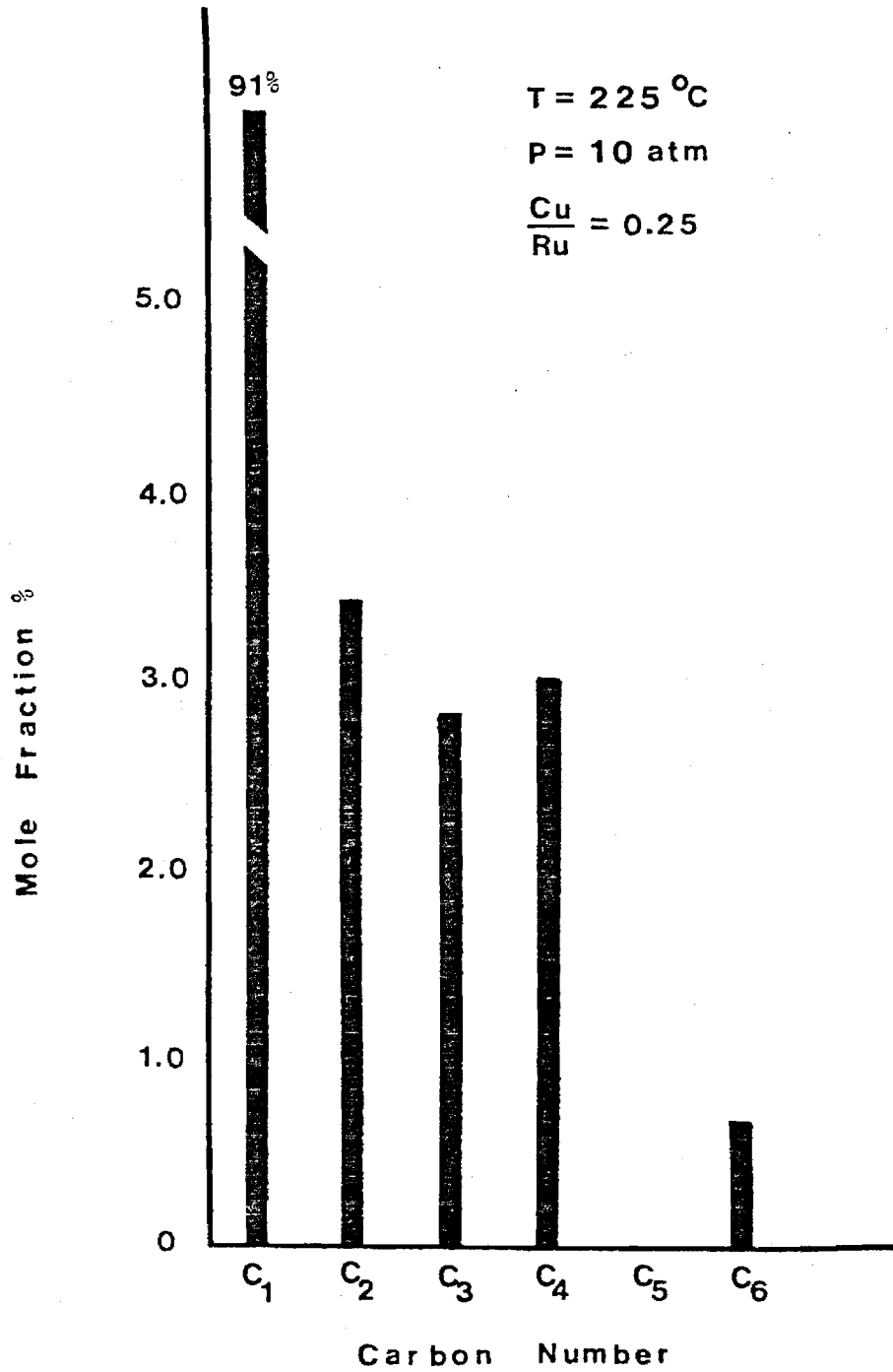


Figure 7. Product Distribution in CO Hydrogenation over 8% Ru - 1.25% Cu/SiO<sub>2</sub> Catalysts at 498<sup>o</sup>K and at 10 atm.

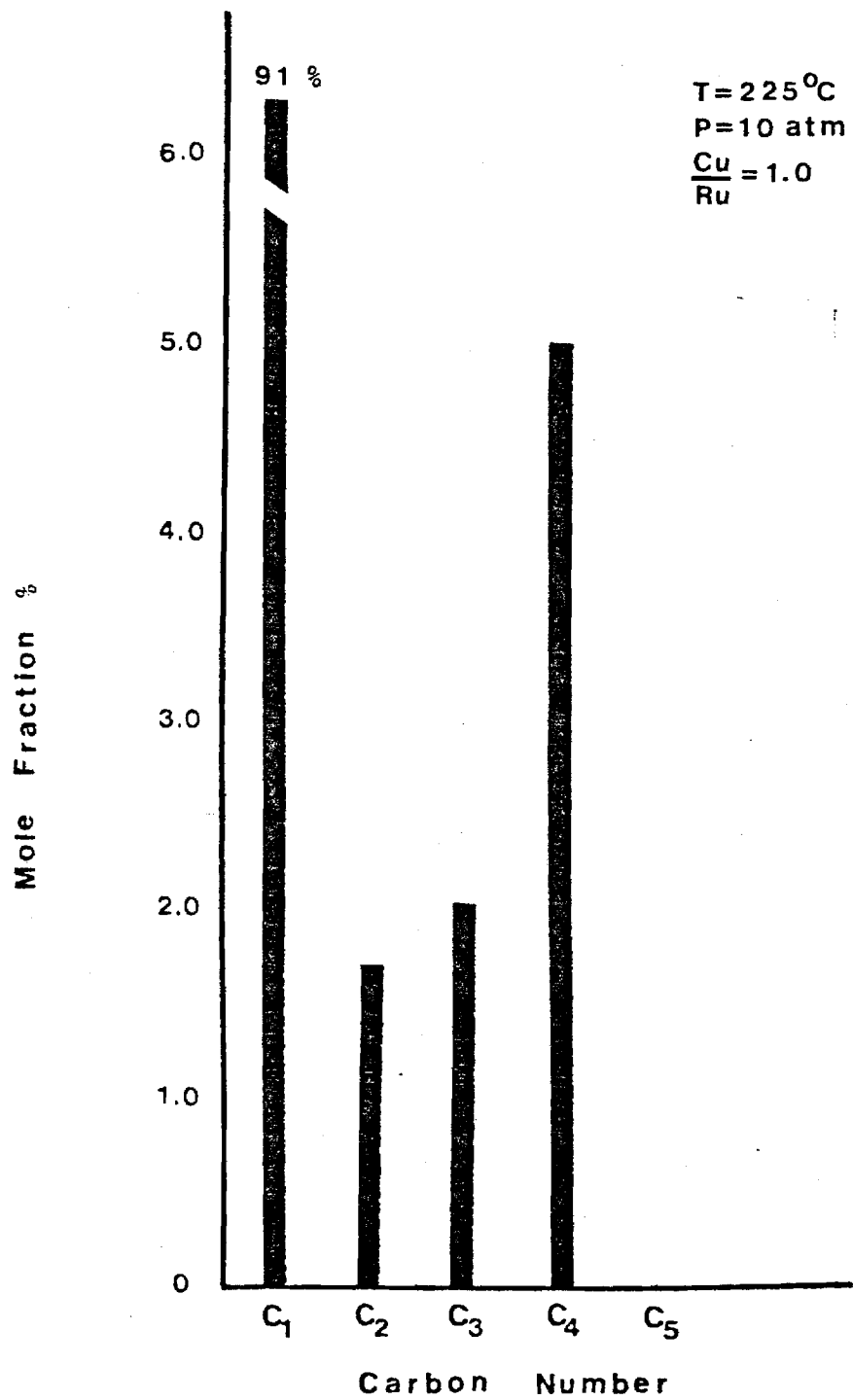


Figure 8. Product Distribution in CO Hydrogenation over 8% Ru - 5.04% Cu/SiO<sub>2</sub> Catalyst at 498°K and at 10 atm.

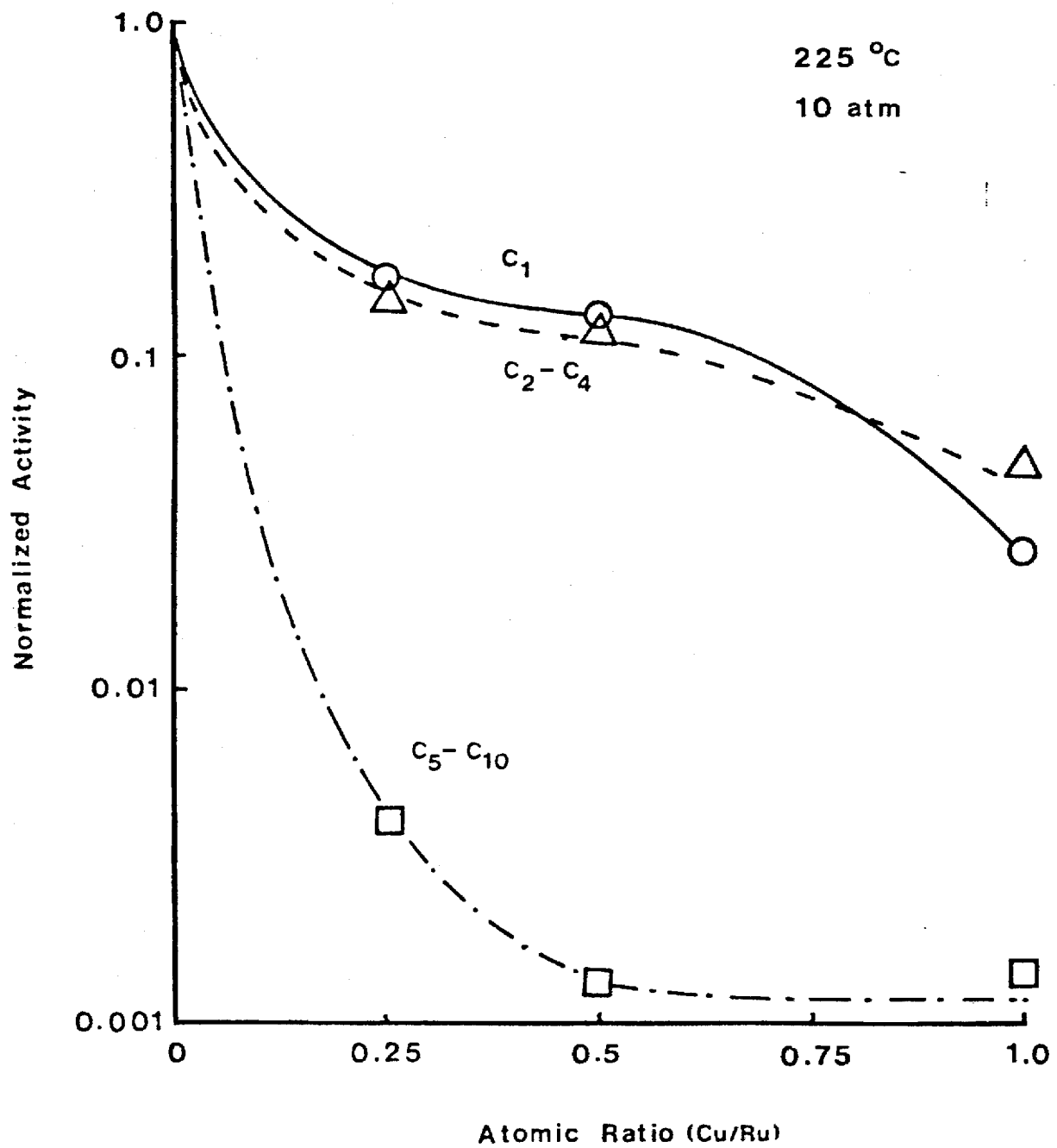


Figure 9. Selectivity in CO Hydrogenation as a function of atomic ratio Cu/Ru for 8% Ru - Cu/SiO<sub>2</sub> catalysts at 498°K and at 10 atm.

whereas  $S_5^+$  decreased by almost two orders of magnitude with an increase in Cu/Ru atomic ratio from 0 to 1. Identical behavior was observed with these catalysts at 523<sup>o</sup>K also.

The results shown in Figure 6 were recalculated using the Equations 2 and 3, and are shown in Figure 10. Again, it is observed that the  $S_{2-4}$  remains relatively constant and does not vary significantly with the Ru loading. However,  $S_5^+$  varies quite significantly with the loading. To summarize the product distribution studies, we have two categories. In one category, only the Ru loading changes (but there is no copper). In the second category, only the Cu loading varies (the Ru loading stays constant at 8 percent). Yet the phenomena of product distribution appears to be similar in both cases: a decrease in Ru loading appears to be similar in nature as an increase in Cu loading.

In addition to methane being the primary CO hydrogenation product over Ru, higher hydrocarbons upto  $C_{10}$  were observed; no oxygenated hydrocarbon products were obtained. The data shown in Figures 4, 5, and 6 indicate that with increased Ru metal loading the selectivity of  $C_5^+$  hydrocarbons is increased dramatically. However, the Ru particle size is independent of the metal loading. Other factors which might influence the formation of higher hydrocarbons is the presence of secondary processes such as readsorption or the involvement of hydrocarbon units bigger than the monomers in the chain-growth process. As we will see below, the operating parameters such as catalyst loading and feed flowrate which might alter the extent of readsorption can be grouped together into a single parameter-fractional CO conversion. Thus, the selectivity  $C_5^+/C_1$  is strongly dependent on the extent of CO conversion.

For Ru-Cu catalysts, however, there are two parameters which might affect the selectivity  $C_5^+/C_1$ . These are (i) the extent of CO conversion, and

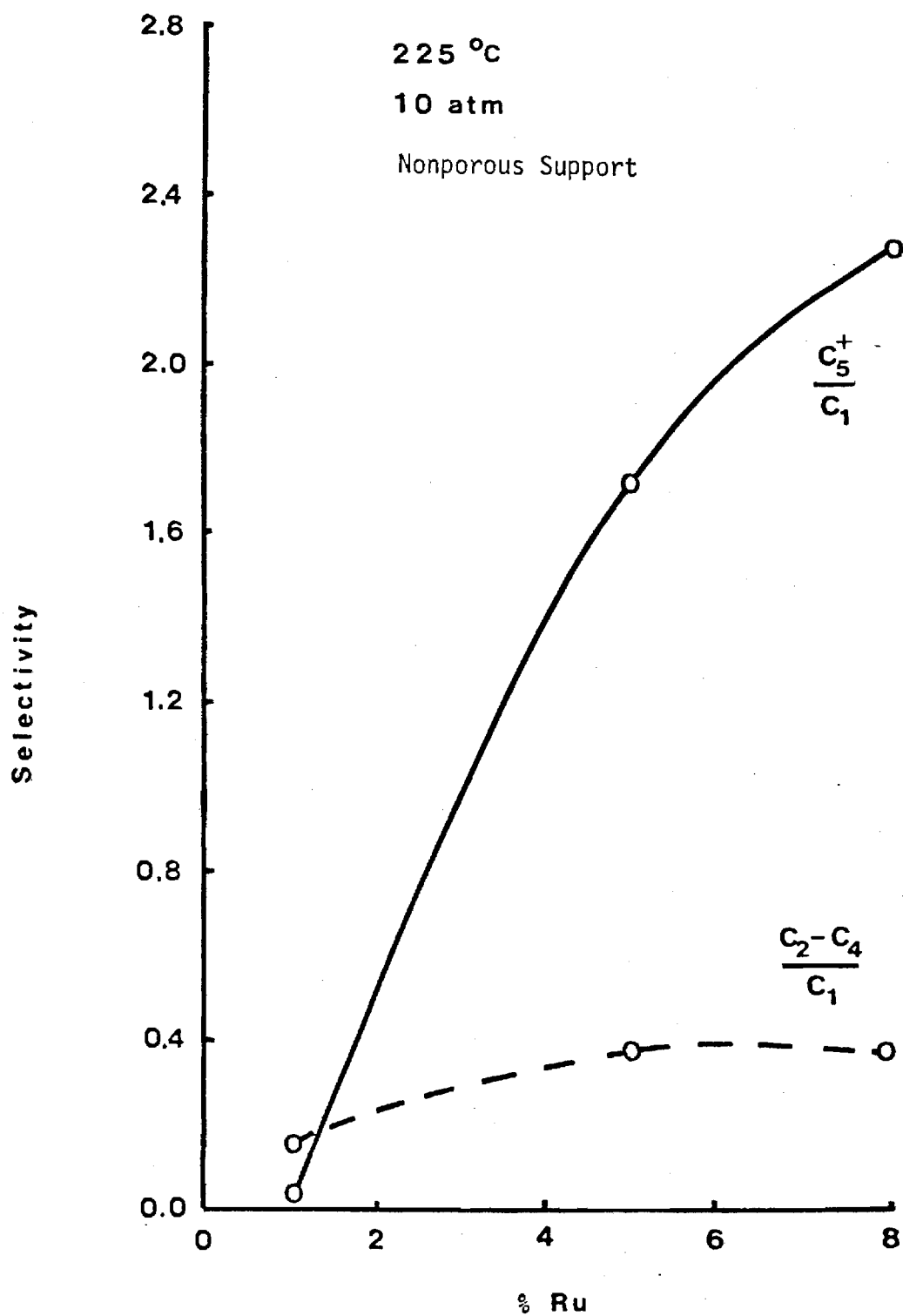


Figure 10. Selectivity for  $C_2-C_4$  and  $C_5^+$  hydrocarbons relative to methane on Cu-free  $Ru/SiO_2$  catalysts at 498°K and at 10 atm.

(ii) the Ru ensemble size. Undoubtedly, the presence of Cu on Ru crystallite will decrease the density of large Ru ensembles to a much greater extent than that of small Ru ensembles. It has been suggested that a minimum particle size (or ensemble size) may be needed for the formation of a large hydrocarbon chain and that this size requirement increases as one desires the hydrocarbon chain of increasing length (34-36). One would thus expect that the presence of Cu on Ru might severely limit the formation of large hydrocarbon chain, as is indeed apparent from the Figure 9.

Thus we have two series of catalysts. In the first series only the loading of Ru is varied and one observes the effect of fractional conversion on the selectivity  $C_5^+/C_1$  of higher hydrocarbons. In the second series, both parameters - the fractional conversion as well as the Ru ensemble size appear to affect the selectivity  $C_5^+/C_1$ . It should then be possible to deduce the effect of ensemble size on the selectivity  $C_5^+/C_1$ . Figure 11 shows the data for both series of catalysts in the form of selectivity  $C_5^+/C_1$  vs. fractional CO conversion. It is quite evident that all the data seem to correlate very nicely on a smooth curve, which suggests that the ensemble size of Ru is not a parameter in the formation of higher hydrocarbons. Had it been a parameter, we would expect the data points for Ru-Cu catalysts to lie below the curve defined by the data points obtained for the catalysts containing Ru only.

Kellner and Bell (33) studied the effect of dispersion on Ru/Al<sub>2</sub>O<sub>3</sub> and found no evidence of a cutoff in chain growth associated with the Ru crystallite size. They suggested that it was possible that such a cutoff could exist for very small particles where the chain-growth probability is distorted by the lack of C<sub>1</sub> monomer units. To confirm that such a cutoff did not exist in the case of Ru-Cu catalyst, we repeated the experiment for the catalyst C4 for which the product distribution is shown in Figure 8. In this repeat

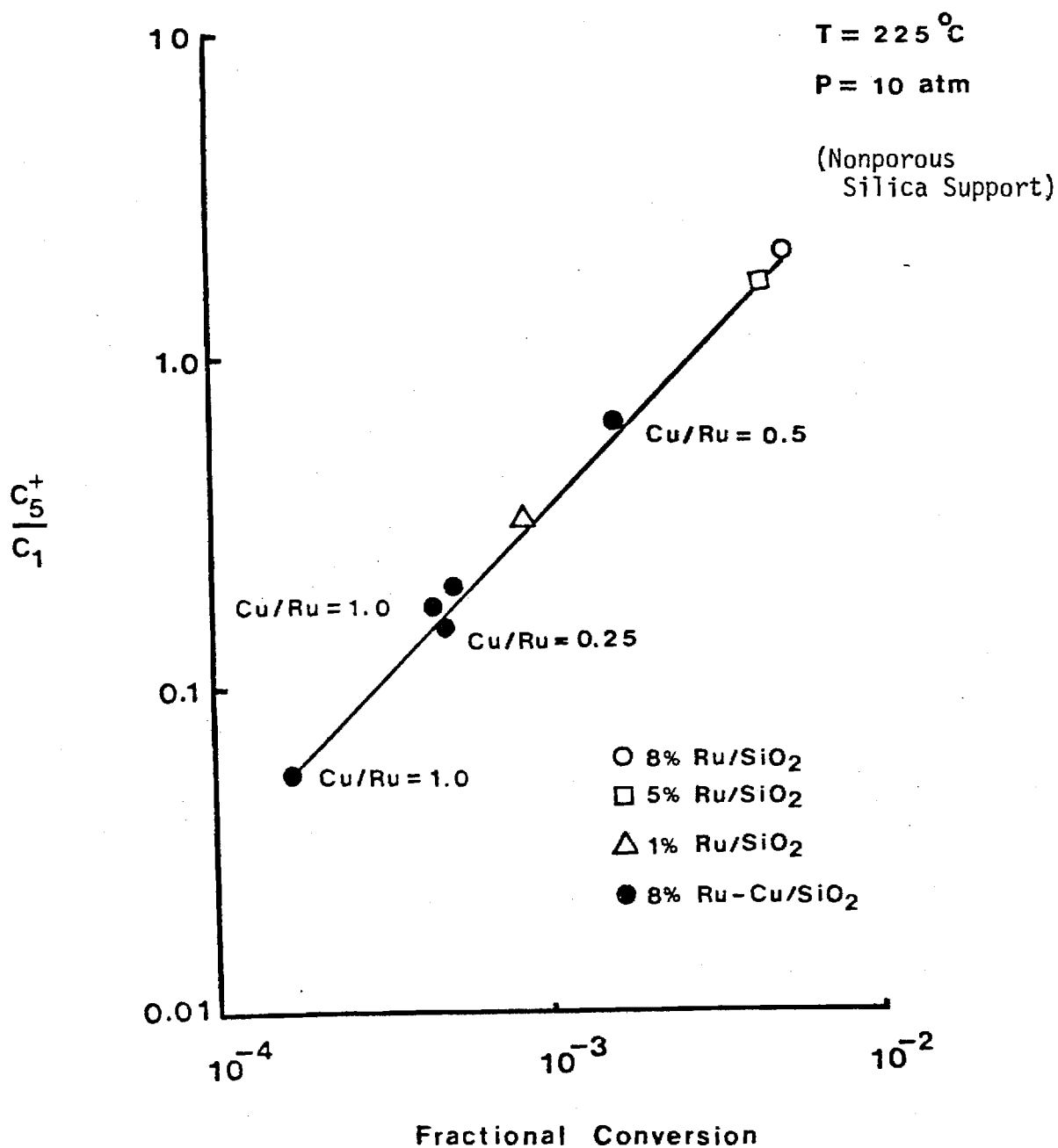


Figure 11. The selectivity  $C_5^+/C_1$  as a function of fractional CO conversion over Ru-Cu catalysts at 498°K and at 10 atm.

experiment, we sought to increase the extent of fractional CO conversion by increasing the catalyst loading and by reducing the feed flow rate. We were able to observe the formation of higher hydrocarbons upto  $C_8$ , clearly indicating the absence of any cutoff in chain-growth.

Nijs et al. (35, 36) investigated the chain-growth over Ru catalysts supported on Y-zeolites and reported the Ru metal particles encage in uniform pore sizes of 1.5 and 3 to 4 nm zeolite Y crystals to terminate the hydrocarbon chain length at carbon numbers (N) of 5 and 12 respectively. If the proposed models for chain-growth in Fischer-Tropsch synthesis via monomer inversion are to hold, the chain growth should not be greatly influenced by the ensemble size. A site just large enough to accommodate the metal-carbon (chain) bond and the monomer should be sufficient for the chain-growth to continue. If the chain-growth takes place vertically with only one end attached to the active surface, then there should be no limit as to how long a chain can be. However, in the case of porous supports, the chain growth might be limited by the pore size (diameter). In our studies, on the other hand, a nonporous fumed silica support was used, thus these "apparent" pore limitations were absent.

To check this hypothesis, we conducted some reaction studies using a porous silica support. Figure 12 shows the product selectivity; the Ru loading was increased from 1% to 8%. It is noteworthy that  $C_2-C_4/C_1$  remains unchanged, just the same as was observed for nonporous silica support. However, the selectivity  $C_5^+/C_1$  increased only 4-5 fold with an 8-fold increase in the Ru loading (compare with Figure 10). Figure 13 compares the nonporous and porous silica-supported Ru catalysts for the variations in the selectivity  $C_5^+/C_1$  vs. fractional CO conversion. It is evident that the effect of

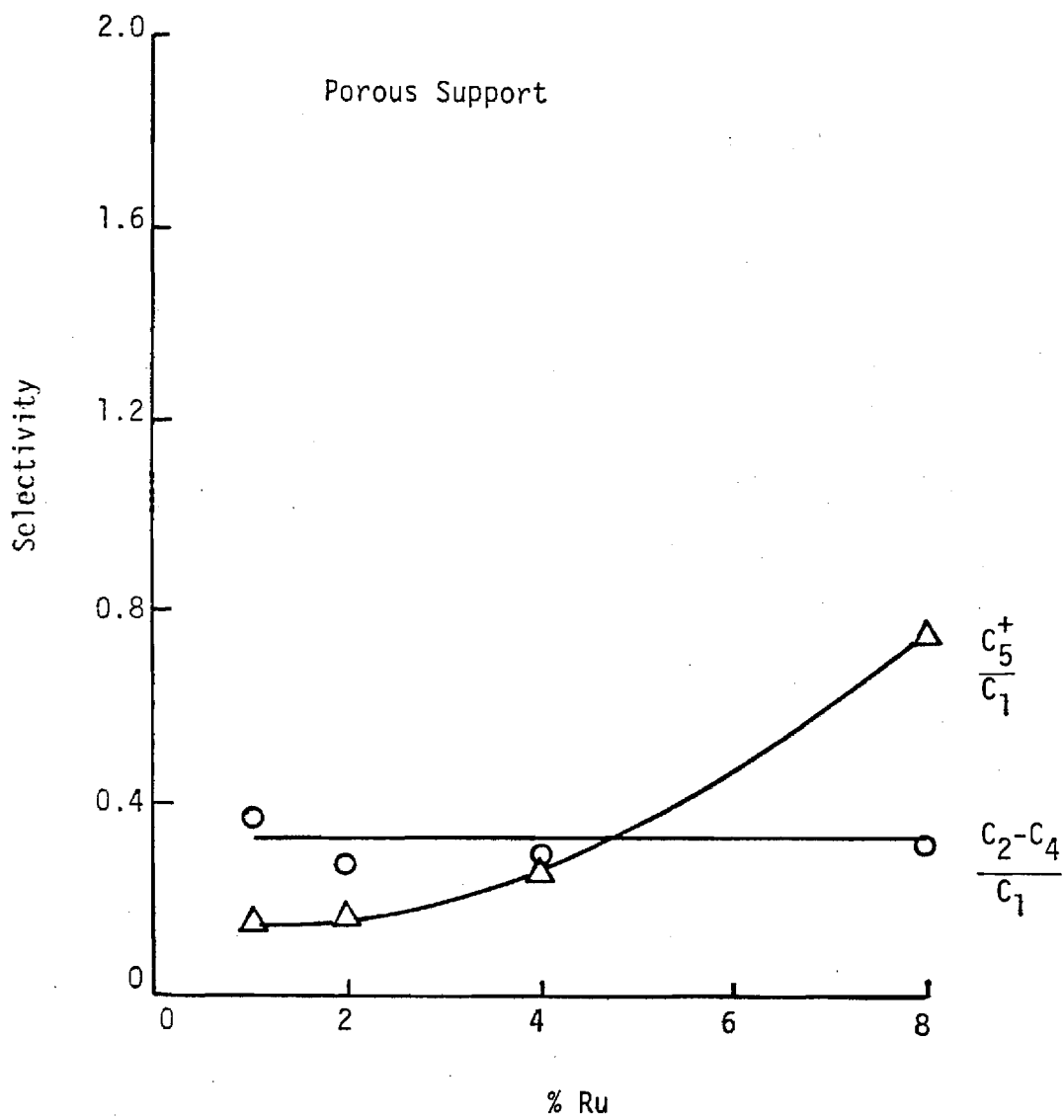


Figure 12. Selectivity for  $C_2-C_4$  and  $C_5^+$  hydrocarbons relative to methane on Cu-free Ru/SiO<sub>2</sub> catalysts at 498°K and at 10 atm.

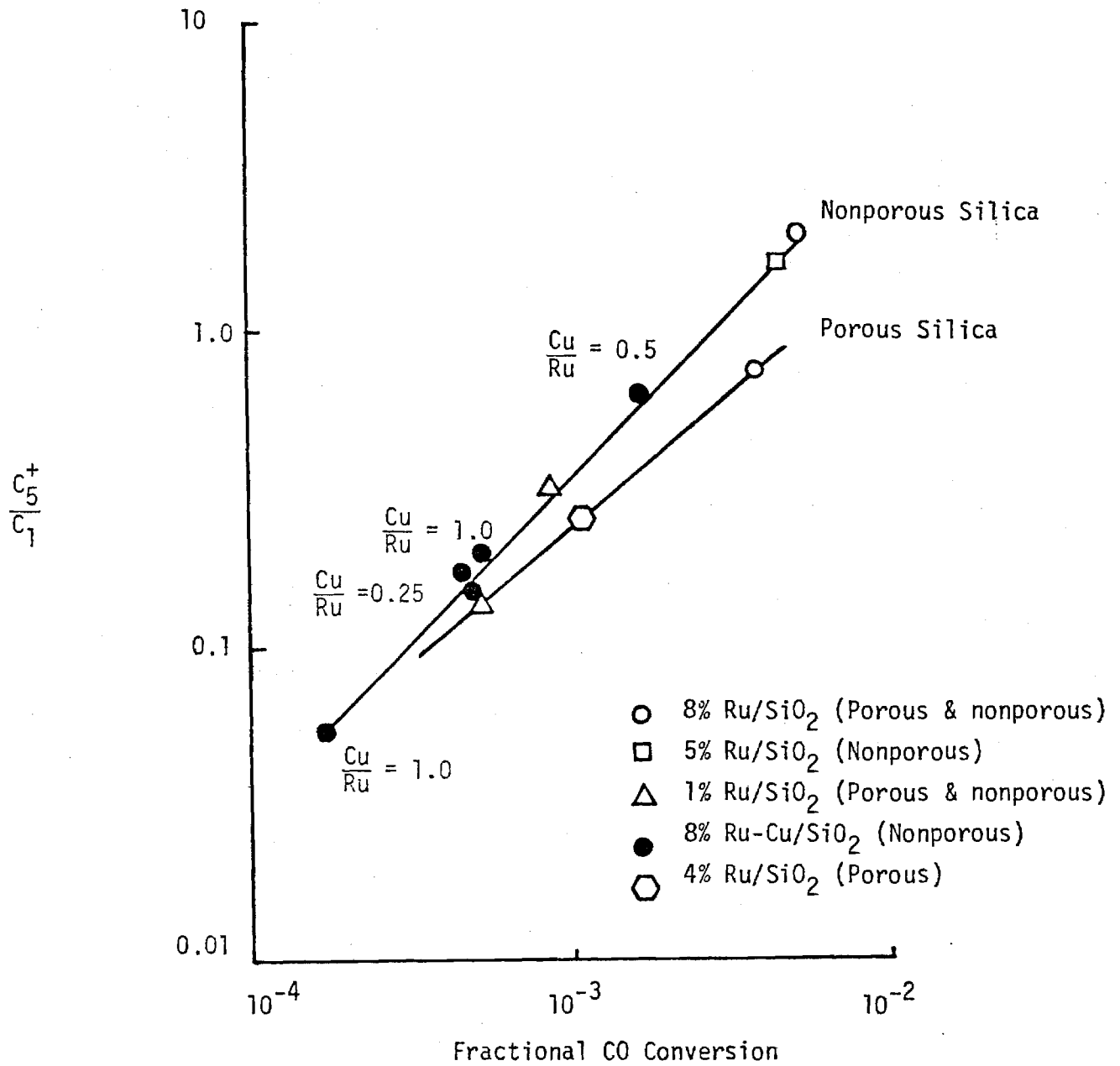


Figure 13. The selectivity  $C_5^+/C_1$  as a function of fractional CO conversion over Ru catalysts supported on porous and nonporous silica at 498<sup>o</sup>K and at 10 atm.

fractional CO conversion on the selectivity is more pronounced for the nonporous silica-supported Ru catalysts. Apparently the pore size (diameter) imposes certain limitations on the chain growth in porous catalysts, a limitation not present in the fumed silica support.

We also studied the effect of Cu on selectivity in porous silica-supported catalysts. The selectivity plot is shown in Figure 14. It is seen that, unlike the observation made in Figure 11 for nonporous silica-supported catalysts, the addition of Cu suppresses the selectivity  $C_5^+/C_7$  as if there were ensemble size effects associated with the presence of copper. We wish to suggest that the presence of copper might reduce the "effective" pore diameter further, thus placing additional restriction on the growth of hydrocarbon chain. Since we have not yet characterized the porous silica support and the catalysts supported on porous silica, we cannot more than speculate at this moment. Further studies will be carried out to check our hypothesis about the role of pore structure in limiting chain growth. The results obtained to date are consistent with this hypothesis, however.

Finally, something needs to be said about the variations in selectivity for the  $C_2-C_4$  and  $C_5-C_{10}$  hydrocarbons. At first glance it would appear that the mechanism for the synthesis of intermediate range hydrocarbons ( $C_2-C_4$ ) is different than the one for the synthesis of higher hydrocarbons. The most commonly used model to describe the product distribution in the Fischer-Tropsch reaction is the Schultz-Flory distribution (4). It is based on the premise that the chain growth occurs in a manner analogous to polymerization process, adding one monomer unit at a time, and that dimers and/or trimers do not undergo this insertion process. The analytical equation is as follows:

$$\ln (M_n) = n \ln \alpha + \ln \left( \frac{1-\alpha}{\alpha} \right) \quad (4)$$

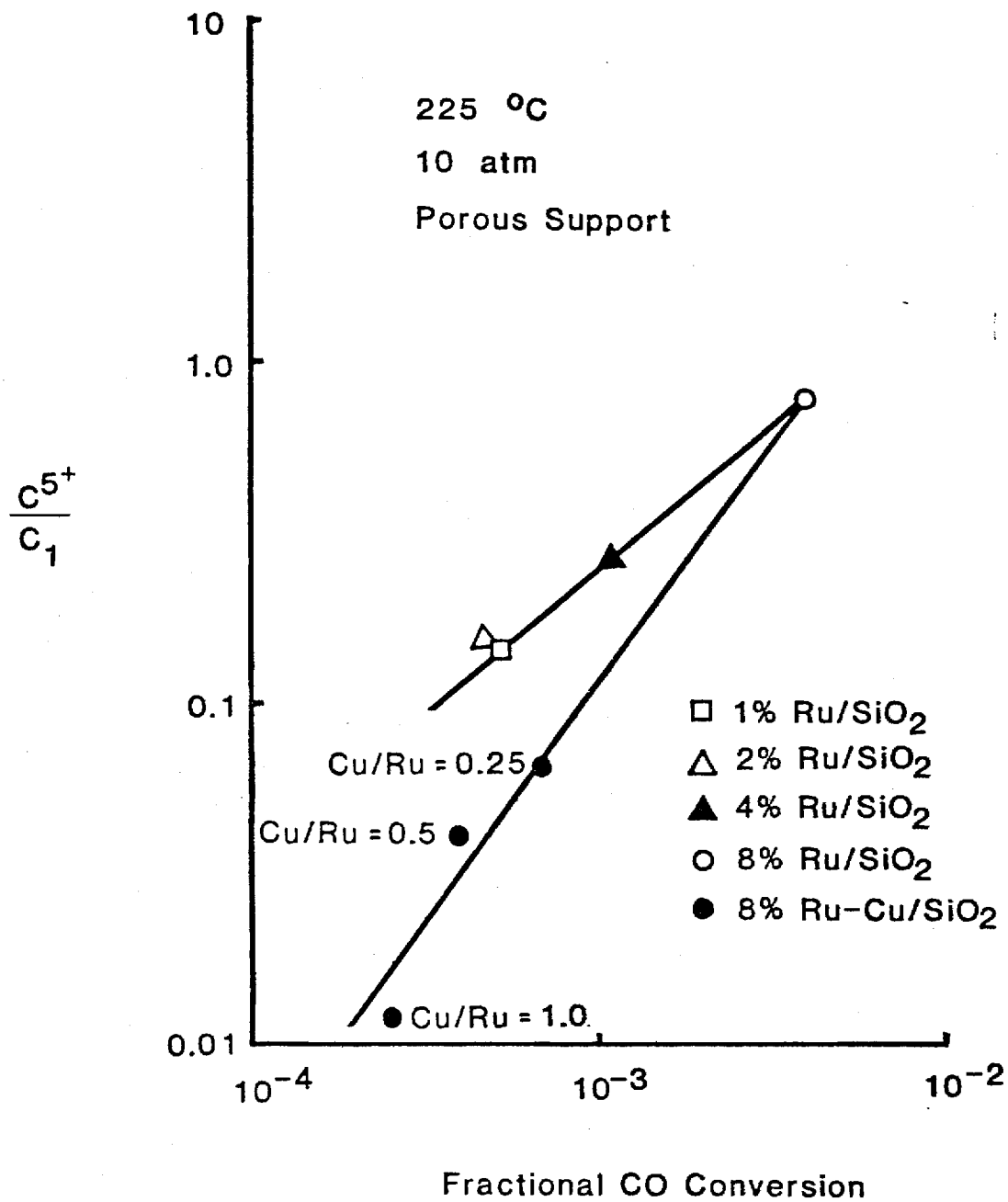


Figure 14. The selectivity  $C_5^+/C_1$  as a function of fractional CO conversion over Ru-Cu catalysts supported on porous silica at 498°K and at 10 atm.

where  $M_n$  represents the mole fraction of the hydrocarbon containing  $n$  carbon atoms, and  $\alpha$  represents the chain growth probability factor. In typical integral reactor operations, the value of  $\alpha$  has been found to vary between 0.65 and 0.80 (1, 2). In one study, it has been suggested that the value of  $\alpha$  increases with increasing fractional conversion, especially when secondary reactions such as readsorption become important (8). Thus, in our work, we could indeed have variations in  $\alpha$  at different fractional conversions. We calculated the selectivity for intermediate range and higher hydrocarbons for a given value of  $\alpha$  using Equation 4. The results of our calculations are summarized in Table V. It is interesting to note that as  $\alpha$  increases from 0.5 to 0.65, the selectivity for  $C_2-C_4$  hydrocarbons increases by about 60 percent whereas that for the  $C_5-C_{10}$  hydrocarbons increases about 300 percent. Hence the results of our work do not necessarily represent a contradiction to the Schultz-Flory Equation. However, an abrupt absence of  $C_5^+$  hydrocarbons rather than a gradual decline in the concentration of higher hydrocarbons suggests that readsorption may indeed be playing a greater role than envisaged in the formation of  $C_5^+$  hydrocarbons. This is another area which we plan to look at more carefully in our future work.

#### REPORTS AND PUBLICATIONS

During the course of this work, two reports have been prepared. The semiannual progress report was submitted on March 1, 1983 and the annual report is being submitted on September 1, 1983. Some of the work described above has been presented at the following two meetings:

- (1) "Bimetallic Supported Clusters in Fischer-Tropsch Synthesis", Presented by P. K. Agrawal at the "Eighth North American Catalysis Society Meeting" held in Philadelphia, PA, May 1-4, 1983.

Table V

Selectivity Variation with  $\alpha$  (Schultz-Flory Equation)

<u><math>\alpha</math></u>	<u><math>C_2-C_4/C_1</math></u>	<u><math>C_5-C_{10}/C_1</math></u>
0.4	1.536	0.2397
0.5	2.250	0.726
0.6	3.144	1.917
0.65	3.666	3.003
0.70	4.242	4.614
0.80	5.568	10.38

- (2) "Bimetallic Supported Clusters in Fischer-Tropsch Synthesis", Presented by P. K. Agrawal at the "57th Colloid and Surface Science Symposium" held at the University of Toronto, Toronto, Canada, June 13-15, 1983.

In addition, this work will be published in the form of two papers. We plan to submit both these papers for publication in the Journal of Catalysis. The first paper is almost in the final manuscript form and will be submitted by September 30, 1983. We hope to have the second paper ready by December, 1983.

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