

"Studies on the Co-Cu-Al₂O₃ Catalyst System for
Conversion of CO and H₂ to Light Hydrocarbon Products"

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INTRODUCTION

Past research efforts on synthesis of hydrocarbons from CO and H₂ have been primarily devoted to two areas: synthesis of liquid hydrocarbons and production of methane (1). Early work was done mainly by Fischer, Tropsch and others in Germany. These researchers tested possible metal compounds in H₂/CO synthesis gas mixtures and they found that compounds of ruthenium, iron, nickel and cobalt were effective under various reaction conditions. They found that iron was the most effective catalyst for formation of liquid hydrocarbons when it was used under medium pressure reaction conditions (2). Recent methanation research showed that nickel was more selective for methane than cobalt, the latter producing more C₂⁺ for the same conversion of CO (3).

Light hydrocarbons can also be produced in the Fischer-Tropsch process (4). CO and H₂ synthesis gas can be produced from coal with existing technology (5,6). By choosing an appropriate catalyst, CO and H₂ can then be used to produce light hydrocarbons as raw materials for the petrochemical industry.

In a previous paper, extensive studies of different catalysts for the conversion of CO and H₂ to light hydrocarbons were reported (7). Among others, a catalyst consisting of cobalt and copper supported on alumina was found to be promising for achieving the above-mentioned objective. In this paper, we report additional studies on this catalyst system. Work included catalyst characterization and testing of various catalyst formulations.

EXPERIMENTAL

The catalysts employed in this study were prepared by a co-precipitation technique. A hot solution of Na₂CO₃ was added to a hot solution of the nitrates of Co, Cu and Al dissolved in distilled water. The precipitate was filtered, washed and finally dried in an oven at 110°C. It was then ground to pass 200 mesh sieve, pelleted, reground and finally sieved, the fraction 14-25 mesh being retained for charges to the catalytic reactor.

In some formulations cupric chloride was used and in others (NH₄)₂CO₃ or NH₄OH was used in the preparation. In two of the latter preparations, Na was added to the oven-dried catalyst by impregnation. A listing of the catalysts is presented in Table I.

Catalyst analyses for Co and Cu were made by a spectrophotometric method. This consisted in dissolving the oven-dried catalyst in concentrated HCl and measuring the solution absorbance for Co at 690 nm and for Cu at 380 nm. Standard solutions were prepared for calibration purposes.

Characterization of a number of catalysts was carried out in a flow microbalance (8). These included measurement of degree of reduction and O₂ adsorption on reduced catalysts. The following sequence was adopted for this purpose:

- 1) Heat in H₂ flow to 450°C.
- 2) Switch to N₂ and cool to room temperature.
- 3) Switch to air and measure weight gain.
- 4) Switch to H₂ and heat to 450°C.
- 5) Switch to air and measure weight gain.

All steps except 3) were run until weight was constant. In step 3), a rapid weight gain was obtained followed by a slow continued gain; this step was terminated after 1/2 hour. The amount of O₂ adsorbed was taken at the break in the curve in step 3).

The amount of reduced metal was calculated from the weight gain in step 5), assuming complete oxidation of the reduced metal was obtained. Overall weight loss in going from the oven-dried state to the reduced state via step 1) was consistently very close to 50% loss for the catalysts tested.

The above sequence was varied to study the effect of reduction temperature and the effect of a low temperature (250°) hold prior to heating to the higher temperature. Also, some adsorptions in step 3) were determined at 0°C instead of room temperature; no difference in initial adsorption was obtained, but the small continued weight gain was suppressed at 0°C.

X-ray analyses were performed on several reduced samples after O₂ chemisorption. Average particle size was estimated by line broadening using the strongest Cu line. Electron microprobe was used to examine Co and Cu distributions in the catalyst. This was accomplished by forming a tablet of the crushed material which after subjecting to reduction, was sliced at the midpoint and carbon-coated. Selected areas were probed for Co and Cu concentrations.

Catalyst activities were measured in a fixed bed reactor. Details are given in the previous paper (7). Catalyst pretreatments were made in-situ in the reactor. Reactor feed consisted of mixtures of H₂ and CO. Product gases were analyzed by gas chromatography for H₂, N₂, CO, CH₄, C₂-C₄ hydrocarbons, C₅⁺ hydrocarbons and alcohols (predominantly CH₃OH). The C₅⁺ fraction consisted of hydrocarbons from C₅ to C₁₀ in decreasing amounts. Condensable liquid collected at room temperature was exclusively water, no measureable alcohols or hydrocarbons being detected.

CO conversion is defined as:

$$\text{CO Conversion} = \frac{\text{CO}_2 + \text{total hydrocarbons} + \text{alcohol}}{\text{CO} + \text{CO}_2 + \text{total hydrocarbons} + \text{alcohol}} \times 100$$

Hydrocarbon selectivities are defined as:

$$\%Y = \frac{Y}{\text{total hydrocarbons} + \text{alcohol}} \times 100$$

where Y represents C₁, C₂-C₄, C₅⁺ or ROH. All values are calculated on a carbon atom basis.

RESULTS

Catalyst Characterization

One CoCu formulation was examined to determine pretreatment conditions appropriate for reduction to the metal and to estimate metal areas. The results are presented in Table II, together with data on a Co catalyst and a Cu catalyst. All tests were carried out starting with oven-dried catalysts. Heating to 450° in H₂ was sufficient to essentially completely reduce the Cu and the CoCu catalyst to the metals; but the Co catalyst was only about one-half reduced under these conditions. Under comparable reduction conditions, the CoCu catalyst showed about a ten-fold larger O₂ chemisorption compared with either the Co or Cu catalyst. On a per gram reduced metal basis, these results translate into a three-fold increase over the Co catalyst and a five-fold increase over the Cu catalyst in surface metal area. A two-stage heating schedule gave larger metal areas (greater O₂ adsorptions) compared to a direct heat up to maximum temperature. This was especially marked at 500°.

Reoxidation of the reduced samples caused changes in metal dispersion. Thus, reduction of the reoxidized CoCu catalyst gave a five-fold loss in metal dispersion. A lesser loss was obtained for the Cu catalyst and no loss was observed for the Co catalyst. Evidently, reoxidation of the reduced catalyst caused sintering of the highly dispersed metal phase. Pretreatment with N₂ in place of H₂ at 450°, followed by reduction resulted in a much lower metal dispersion, being only slightly greater than the reoxidized sample. Also, total reduction was somewhat lower (79%). Assuming all the Cu had reduced, this corresponds to about 50% reduction of the Co,

close to that obtained with the Co catalyst. Evidently, N_2 pretreatment is equivalent to air oxidation in causing metal sintering and Co interaction with the support.

X-ray analyses of reduced samples exposed to air showed Cu metal to be the major component, with Cu_2O as a minor component. The amount of Cu_2O relative to Cu was greater for those catalysts which had high O_2 adsorptions and negligible for low uptake catalysts. This indicates some surface oxidation of Cu occurred during exposure to air. The Co catalyst contained appreciable amounts of $CoAl_2O_4$ in addition to Co metal, accounting for its incomplete reduction. On the CoCu catalysts, a separate Co metal phase was not detected by x-ray analysis.

Estimates of average particle size from x-ray line broadening generally agreed with the O_2 adsorption results. Although average particle sizes based on adsorption did not give good quantitative agreement with the x-ray values as seen in Table II, the trends are nevertheless in the same direction. Uncertainties in the exact stoichiometry of adsorption and possible oxidation beyond the monolayer probably account for these differences.

Electron microprobe examination of the CoCu catalyst showed the distribution of Co and Cu across the pellet to be quite inhomogeneous, with some areas high and others low in concentrations of metals. However, in general, Co and Cu were located in the same vicinity.

Catalyst Activity

A complete product analysis for a typical run is presented in Table III. Hydrocarbon products were predominately normal straight chain molecules, small amounts of isomers only appearing at high conversions. Generally, olefin/paraffin ratios were low for C_2 , about one for C_3 and low for C_4 compounds. The alcohol was exclusively methanol; small amounts of ethanol were only detected after prolonged reaction at high conversions.

Table IV shows the results of different pretreatments. The catalyst pretreated with H_2 at $520^\circ C$ was more active for converting CO than the catalyst air calcined at $520^\circ C$, then reduced in hydrogen at $275^\circ C$. The catalyst that was held in hydrogen at $225^\circ C$ for four hours, then at $520^\circ C$ for another four hours was even more effective. However, hydrogen at high pressure with the two-stage temperature schedule during the pretreatment had an adverse effect on conversion of CO. Different pretreatment methods did not have much effect on hydrocarbon product selectivities.

Table V shows that increased sodium on catalysts caused a decrease in CO conversion; however, the relationship between sodium content and CO conversion was not linear. The two percent addition of sodium had the largest effect on CO conversion. The product selectivities were likewise affected, alcohol decreasing and the C_5^+ fraction increasing with sodium content.

Catalysts prepared with $CuCl_2$ were less active than those with $Cu(NO_3)_2$. Table VI compares two pairs of otherwise identical catalysts. In both cases, the catalysts prepared from the chloride had lower conversions, and lower C_5^+ and ROH selectivities. However, they had higher CH_4 selectivities.

The effects of process variables on conversion were briefly studied with one catalyst formulation; the results are given in Table VII. Larger conversions were obtained at higher temperature and H_2/CO ratio, while pressure had little effect. Selectivity-wise, the following trends were observed: (1) increase in temperature - higher C_2-C_4 and C_5^+ and lower CH_4 and olefin/paraffin ratio; (2) increase in H_2/CO ratio - lower olefin/paraffin ratio; (3) increase in pressure - no effect.

The effect of catalyst composition was studied in some detail. Figures 1 and 2 give conversions and selectivities for one run condition. Other run conditions gave similar trends. Conversion was found to correlate best with total metal loading. Conversion reached a maximum at a total loading around 18%. Thereafter, conversion levelled off or decreased slightly with increasing metal content. Production of CO_2 appeared to be closely related to CO conversion. Hydrocarbon selectivities correlated best with metal ratio. At one extreme, the Co catalyst

produced a high percentage of CH₄ and no ROH. As the fraction of Cu increased, CH₄ decreased and ROH increased. Of significance, C₂-C₄ was higher over a wide range of catalyst compositions. The C₅⁺ fraction showed a similar trend. At the other extreme, the Cu catalyst gave high ROH with only a small percentage of CH₄ and C₂-C₄.

DISCUSSION

Catalyst Characterization

It is evident that Co and Cu interact during the prereduction step. The presence of Cu engendered reduction of the Co. The two together resulted in a much greater metal dispersion than each one separately. Sinfelt, (9) found a similar effect for RuCu and OsCu catalysts. Reoxidation caused appreciable sintering of the highly dispersed metals. Hence, air regeneration of aged catalysts would most likely cause a severe deactivation of the original catalyst activity.

The degree of dispersion was greatly affected by the pretreatment used. Oxidized and N₂ treated catalysts gave low metal dispersions after high temperature reduction, whereas direct treatment of the oven-dried catalysts with H₂ during heating gave much better dispersions. In the latter case, the heating schedule was important, viz., holding at 250° before subsequent high temperature heat-up resulted in even higher dispersions. Similar improvement in metal dispersion was found for Ni catalysts (10). Evidently, slow heating results in formation of small metals crystallites which are then stable at the higher temperatures. Increased metal dispersions were reflected in higher catalyst activities for CO conversion.

The increased dispersion found in H₂ pretreatment may be due to formation of an alloy phase or stable surface bimetallic clusters (11). The x-ray and electron microprobe results are in accord with this viewpoint. These states may be more stable towards sintering than crystallites of the individual metals. Further research along these lines is in progress and will be reported at a later date.

Catalyst Reactivity

Temperature had the most profound effect on catalyst activity and reaction path. Thus, at 250° and below, conversions were low and the major products were hydrocarbons and water; whereas at 275° and higher, conversions were high with formation of hydrocarbons and carbon dioxide. This is more or less typical of cobalt-containing Fischer-Tropsch catalysts (12).

At a given set of conditions, catalyst conversions increased with metal loading, as expected. However, the increase was not linear indicating that the amount of active metal surface area was not entirely proportional to the total metal present. Differences could reside in variations in degree of reduction and metal dispersion achieved for the various loadings. This is especially evident at the higher loadings, where conversions were found to tail off. The latter effect may be due to sintering of the basic metal crystallites to larger-sized particles.

The addition of copper as a promoter in Fischer-Tropsch catalysts was reported to facilitate reduction of the metal components, but not alter activity or selectivity (12). In addition to improving the reduction of Co, our CoCu catalysts also gave differences in selectivities. Thus, the Co catalyst gave selectivities relatively high in CH₄, low in C₅⁺ and no ROH; whereas, the Cu catalyst gave predominately ROH (Figure 2). In contrast, the CoCu catalysts gave moderate selectivities for CH₄ and C₅⁺ and low ROH. The significant selectivity improvement with the CoCu catalyst was in the C₂-C₄ range, which approached close to 50% of the hydrocarbon product. Although product selectivities changed somewhat with increase in Cu to Co ratio, the C₂-C₄ selectivity was relatively insensitive to this parameter. The major effect was to decrease the C₅⁺ and increase the ROH selectivities.

The addition of sodium to the catalyst had a depressing effect upon conversion. In addition, the C₅⁺ selectivity increased while the ROH decreased. Sodium

addition to a Co:Cu (9:1) catalyst was reported to be unfavorable (13), resulting in increased molecular weight of products and rapid catalyst decline. Since most of the catalysts were prepared using sodium carbonate as the precipitant, some sodium may have been retained by the catalysts after washing. Comparison of conversions (Figure 1) indicates that up to 1% Na may have been present in the normally prepared catalysts. It appears that the sodium-free catalyst is somewhat more active.

The use of CuCl_2 in place of $\text{Cu}(\text{NO}_3)_2$ in the preparation had an interesting effect on catalyst performance. A decrease in conversion was accompanied by a decrease in ROH selectivity, strangely parallel to the effect of added sodium. The reason for this effect is not known at present.

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Table I. Catalyst Compositions

No. ^a	wt. % ^b		Remarks ^c
	Co	Cu	
2	0	0	Al ₂ O ₃ only
3	8.5	0	
4	0	13.0	
5	7.8	11.0	
7	7.1	8.8	
10	5.1	4.0	(NH ₄) ₂ CO ₃ used
17	7.5	4.9	
18	8.1	16.1	
19	7.4	1.3	
33	7.3	0	
34	0	12.3	
37	9.8	8.1	
38	6.4	8.8	
42	5.5	15.5	
43	5.0	3.4	NH ₄ OH used
44	4.8	3.6	NH ₄ OH used, 2% Na ₂ O added ^d
51	5.6	3.9	NH ₄ OH used, 1% Na ₂ O added ^d

^aCatalysts above dotted line prepared with CuCl₂ and those below with Cu(NO₃)₂.

^bOven-dried basis

^cNa₂CO₃ used for precipitation except where otherwise noted.

^dImpregnation

Table II. Effect of Pretreatment on Metal Dispersions

Catalyst	Pretreatment ^a °C	Metal Reduced, %	Weight O ₂ Chemisorbed, b mg/g	Average Metal Adsorption	Particle Size, Å XRD ^d
2	-/450	0	0		
3	250/450	46	1.5(1.5) ^e		
4	250/450	94	2.5(1.5) ^e	130(220) ^e	90(150) ^e
5	250/450	96	19.0(3.5) ^e	25(140) ^e	50(100) ^e
5	250/400	-	22.0	20	30
5	-/400	-	16.5	30	40
5	250/500	-	24.0	20	40
5	-/500	92	10.8		
5	450 ^f /450	79	4.5	90	130

^aH₂ used; 2h hold at each temperature.

^bcatalyst charge basis (oven-dried).

^cbased on ratio of weights of O₂ chemisorbed to redox change assuming one O per metal site.

^dby x-ray diffraction line broadening.

^eafter high temperature oxidation-reduction cycle.

^fN₂ used.

Table III. Analysis of Reaction Products

<u>Component</u>	<u>Volume, %</u>	<u>Selectivity, %</u>
H ₂	55.3	
N ₂	0.18	
CO	22.6	
CO ₂	0.18	
CH ₄	3.06	46.0
C ₂ H ₄	0.021	}
C ₂ H ₆	0.135	
C ₃ H ₆	0.157	
C ₃ H ₈	0.178	
C ₄ H ₈	0.034	
C ₄ H ₁₀	0.108	28.4
C ₅ ⁺	0.30	22.3
ROH	0.22	3.3
H ₂ O	0.40	

CO Conversion % 23.2

CO₂, % 2.7

Olefin/Paraffin 0.53

Catalyst 38, 18.47 g charge

Reaction conditions: 235°, 750 psig, 3H₂/CO, 7.14 cc/sec

Table IV. Effect of Pretreatment on Conversion

Pretreatment ^a : Catalyst	CO Conversion, %			
	A	B	C	D
7 ^b	37	58		
38 ^c		17	38	16

^aPretreatments:

A - (1) air, 520°, 4 hr. (2) H₂, 275°, 2 hr., 5 psig.

B - (1) H₂, 520°, 4 hr., 5 psig.

C - (1) H₂, 225°, 4 hr. (2) H₂, 520°, 4 hr., 5 psig.

D - (1) H₂, 225°, 4 hr. (2) H₂, 520°, 4 hr. 60 psig.

^bReaction conditions: 275°, 750 psig, 2H₂/CO, 0.77 cc/g sec.

^cReaction conditions: 250°, 750 psig, 2H₂/CO, 0.77 cc/g sec.

Table V. Effect of Sodium on Catalyst Activity

Catalyst	43	51	44
Na ₂ O, %	0	1	2
CO Conv., % ^a	22	19	2
<u>Selectivity</u>			
C ₁	36	37	37
C ₂ -C ₄	36	40	33
C ₅ ⁺	18	21	30
ROH	10.	2	0

^aReaction conditions: 275°, 500 psig, 2H₂/CO, 0.77 cc/g sec.

Table VI. Effect of Copper Salt on Catalyst Activity

Pair	1		2	
	Catalyst	10	43	7
Cu salt ^a	Cl	NO ₃	Cl	NO ₃
CO Conv., % ^b	9	39	59	90
<u>Selectivity</u>				
C ₁	42	35	40	26
C ₂ -C ₄	45	38	41	42
C ₅ ⁺	13	19	18	26
ROH	0.2	8	2	6

^a Used in catalyst preparation

^b Reaction Conditions: 275°, 750 psig, 2H₂/CO, 0.77 cc/g sec

Table VII. Effect of Process Variables on Conversion

Values are CO Conv., %

Temp., °C	235		250	
	H ₂ /CO	3/1	1/1	3/1
Pres. psig	750	34	13	77
	1000	41	10	37
			-	29

Catalyst 38, 0.38 cc/g sec

FIG. 1
 CATALYST CONVERSION VERSUS METAL LOADING - RUN 1

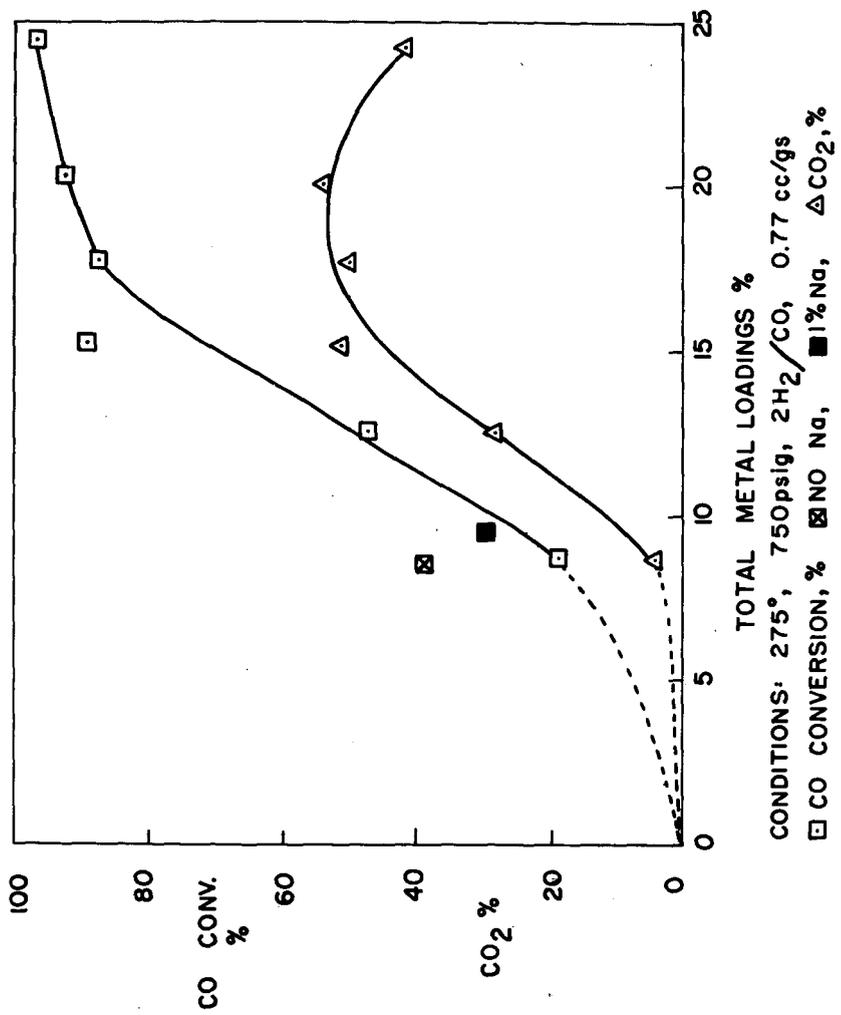
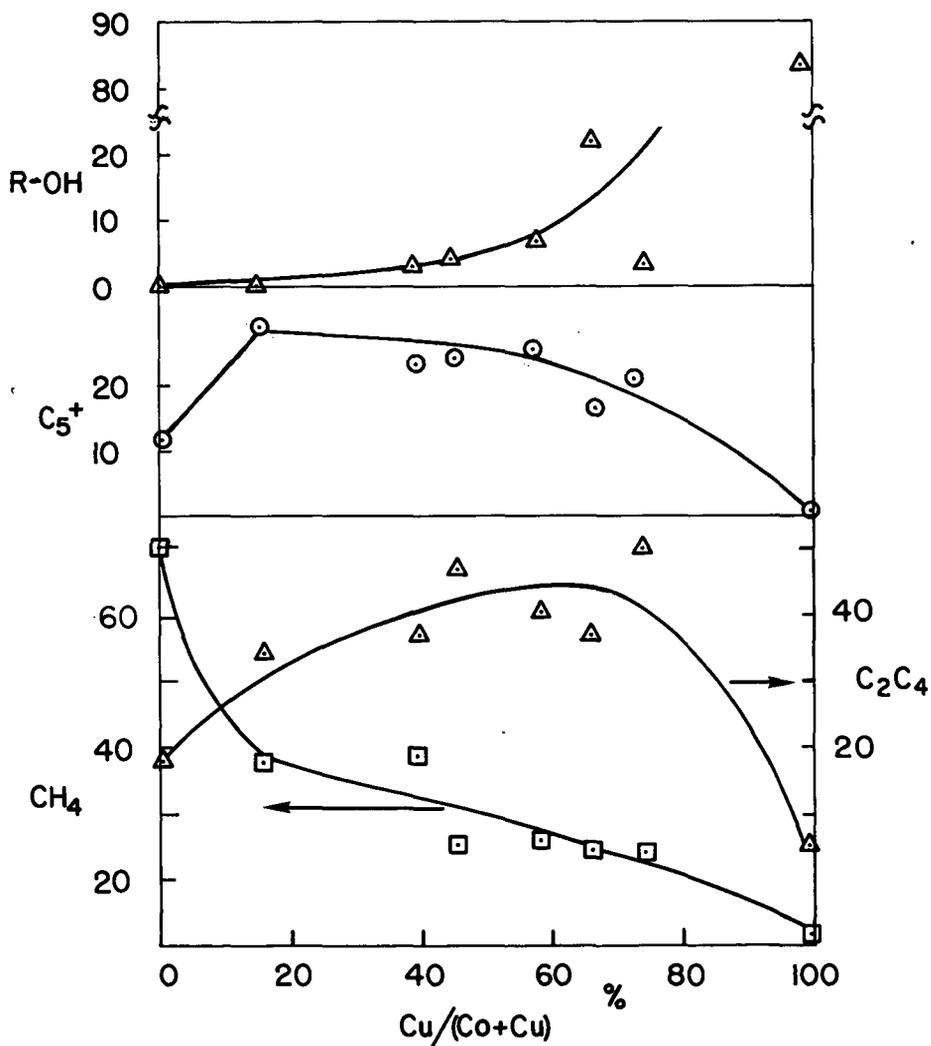


FIG. 2
 CATALYST SELECTIVITIES VERSUS WEIGHT FRACTION COPPER - RUN 1



CONDITIONS: 275°, 750psig, $2\text{H}_2/\text{CO}$, 0.77 cc/gs