

"The Synthesis of Light Hydrocarbons from CO and H₂ Mixtures over Selected Metal Catalysts"

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INTRODUCTION

The synthesis of hydrocarbons and oxygen containing organic chemicals by reaction of CO and H₂ over catalysts has been investigated extensively in the past. This work is summarized in a number of review papers (1-4). More recently a number of workers have been active in investigation of these reactions (5-9). In this extensive previous literature no particular emphasis was given to the preferential production of lower molecular weight hydrocarbons. Mostly the previous work has been concerned with the formation of methane and C₅ hydrocarbons and oxygenated derivatives. There is an exception to this in the extensive work done in Germany on isobutylene production in the Isosynthesis Process (10).

It, therefore, was thought to be worthwhile to reinvestigate the possibilities for the specific production of C₂-C₄ materials with de-emphasis on the production of CH₄ and C₅ substances or their elimination as products, if possible. This route might open up new sources of C₂-C₄ hydrocarbons for use in the important petrochemical industry which in recent years has been moving in the direction of heavier feed stocks to meet the demands for ethylene, propylene and C₄ hydrocarbons (11).

This paper is a first of a series of publications from this laboratory on the production of C₂-C₄ hydrocarbons from CO/H₂ mixtures and deals with exploratory research on a variety of known Fischer-Tropsch catalysts. Using the literature as a guide a number of catalysts were prepared and tested. Reaction conditions, temperature, pressure, gas flow rate and H₂/CO ratio of the feed gas were preliminarily investigated to select the most promising regime for study of the chosen catalysts. The catalysts chosen for testing were Fe, Co, Ni, Cu, and ThO₂. The catalysts preparation, testing procedures and the results obtained are presented in this paper.

EXPERIMENTAL

I. Catalyst

The catalysts tested in these studies were prepared by coprecipitation and impregnation methods. Compositions of the catalysts are based on the quantities of metal salts used in the preparation assuming complete precipitation or in the case of impregnation, complete adsorption of the aqueous solutions used. More complete compositional analysis of the catalysts are now being done by analytical methods. Table (I) contains information on the catalysts tested.

II. Description of Catalyst Testing Equipment

The reactor flow diagram is shown in Figure 1. Carbon monoxide-H₂ mixtures prepared by Linde Speciality Gas Division of Union Carbide Co., were used. The H₂/CO ratios were 1/1, 3/2, 2/1, 7/3, and 3/1.

The reactor was made of 314 stainless steel tubing, one foot long having an outside diameter of 1 inch and an inside diameter of 0.5 inch. A 1-inch thick aluminum shield was placed around the reactor tube to insure even temperature distribution in the reactor. Catalysts were loaded in the middle section of the reactor tube and ceramic spacers were used before and after the catalysts bed. One thermocouple was used to measure the catalyst bed temperature and another thermocouple was used to measure the temperature of the aluminum shield. The thermocouple in the aluminum shield was connected to a temperature controller. There was less than an 0.5°C difference between the two measured temperatures when the reaction conditions

reached equilibrium.

The catalysts were oven dried at 110° C, ground to pass through a 200-mesh sieve and then tabletted into pellets. These pellets were later crushed to -14, +25 mesh size before loading in the reactor. The reaction variables were adjusted to the desired temperature, pressure, and input flow rate prior to sampling of products. Gas samples were taken at appropriate times and injected directly into chromatograph columns for analysis.

III. Analysis and Calculation of Results

A molecular sieve 5A column was used to analyze H₂, N₂, CO and CH₄. Silica gel was used to analyze H₂, CO₂ and C₂H₆. An activated alumina column with F.I.D. was used to analyze light hydrocarbons (12). A carbowax 1500-teflon column was used to analyze water and alcohols. An OV-17 column was used to analyze liquid hydrocarbons. Liquid condensate was captured in a cyclone separator and a room temperature collector. Reaction conditions were adjusted to minimize production of liquid hydrocarbons. At times small amounts were produced; these were recovered and analyzed. The C₅ fraction was analyzed using an activated alumina column as the G.C. oven was heated up to 370° C. These products came out in sequence of carbon atom number, the amounts decreasing with molecular weight.

Calculation of an accurate material balance was not possible since we did not have integrator equipment on the input flow. Consequently, all calculations are on an output basis. This will lead to small errors only since considerable care was taken to obtain complete recovery and accurate analysis on the product. Calculations of conversion and selectivities were done by computer on the basis of carbon atom balance. Water was collected as a liquid product but was not included in the conversion or selectivity calculations. At a later date water will be included in the analysis when material balances are possible.

CO conversions were calculated in the following manner:

$$X = \text{CO} + \text{CO}_2 + \sum_{i=1}^{10} i\text{C}_i\text{H}_{2i+2} + \sum_{i=2}^{10} i\text{C}_i\text{H}_{2i} + \sum \text{alcohols}$$

(all in the product gas)

$$Y = \text{CO}_2 + \sum_{i=1}^{10} i\text{C}_i\text{H}_{2i+2} + \sum_{i=2}^{10} i\text{C}_i\text{H}_{2i} + \sum \text{alcohols}$$

(all in product gas)

$$C_5^+ = \sum_{i=5}^{10} i\text{C}_i\text{H}_{2i+2} + \sum_{i=5}^{10} i\text{C}_i\text{H}_{2i}$$

$$\text{CO conversion \%} = \frac{Y}{X} \times 100$$

Selectivities for different product fractions are calculated as:

$$\text{CO}_2\% = \frac{\text{CO}_2 \text{ in product gas}}{Y} \times 100$$

$$\text{CH}_4\% = \frac{\text{CH}_4 \text{ in product gas}}{Y} \times 100$$

$$C_2-C_4 = \frac{C_2-C_4 \text{ in product gas}}{Y} \times 100$$

$$C_5^+ \% = \frac{C_5^+ \text{ in product gas}}{Y} \times 100$$

$$O/P = \frac{C_2H_4\% \times 2 + C_3H_6\% \times 3 + (1C_4H_8\% + 2C_4H_8\% + i C_4H_8\%) \times 4}{C_2H_6\% \times 2 + C_3H_8\% \times 3 + (nC_4H_{10}\% + i C_4H_{10}\%) \times 4} \times 100$$

$$R-OH\% = \frac{\Sigma \text{ alcohols in product gas}}{Y} \times 100$$

The composition analyses carried out and calculated as described are thought to be quite reliable. At the present state of development the reproducibility and accuracy of the results are estimated to be within $\pm 3-5$ units on the percentages given.

RESULTS AND DISCUSSION

While the literature dealing with carbon monoxide hydrogenolysis is quite voluminous on the metals we have chosen for study, it is difficult if not impossible to determine their relative effectiveness for the particular products of interest in our research. Also catalysts of interest for our purposes are all not commercially available so it was necessary to synthesize our own as well as use commercially available catalysts. Likewise, the literature of Fischer-Tropsch is a rough guide only in choice of reaction conditions for our studies. It was necessary to carry out a number of preliminary studies to orient our program to suitable temperatures, pressures, H_2/CO ratios and flow rates. The synthesis is highly exothermic, consequently conversion rate must be adjusted so that temperature rise is not excessive in small catalyst bed. Temperature proved to be the most important variable influencing conversion and once the temperature range was set the ranges of the other variables were chosen not only for processing reasons but also for convenience in experimentation, handling of materials and minimizing the use of feed gases.

Iron Catalyst

Referring to Table II a number of conclusions are apparent. Iron catalysts after proper reduction and nitriding are very active for reduction of CO at the conditions chosen. Catalyst 26 was so active that the temperature of the catalyst rose to $260^\circ C$ instead of $225^\circ C$ which was intended at the beginning of the run. These catalysts give low methane production relative to C_2-C_4 and give the lowest CH_4/C_2-C_4 ratio of all the catalysts tested. The amount of CO disappearing to C_5^+ is also modest as is the production of R-OH. Notably outstanding for the iron catalysts is the high olefin/paraffin ratio of the C_2-C_4 hydrocarbon. The iron catalysts generally give high CO_2 yields. This was expected since iron is known to be a good catalyst for the water gas shift reaction. Iron catalyst 22 prepared by precipitation of the nitrate and containing copper as a promoter was not active at $225^\circ C$. However, it became quite active at $265^\circ C$ (Table III).

Catalysts 22 and 26 contain copper as a promoter, however, the activities and product distributions of these catalysts are comparable with iron alone on Kieselguhr (23) and sintered iron synthetic ammonium catalyst (ICI). The latter was very active and altogether gave the most favorable product distribution of all catalysts tested. The effect of copper on iron catalyst is not known at this time and is a subject for further work.

Table III gives further data on iron catalysts. Catalyst (ICI) was given two different reduction treatments. Pretreatment by reduction in H_2 at $550^\circ C$ followed by nitriding with NH_3 at $325^\circ C$ gives a catalyst which is more active than pretreatment with H_2 at $450^\circ C$ (temperature required for similar conversion was $25^\circ C$ higher than that for the same catalysts with pretreatment b). The important difference here is the step of nitriding in the pretreatment step. Such a step is known to make iron catalysts more active for Fischer-Tropsch synthesis (13,14).

Data in Table III for catalyst 22 shows the effect of temperature on catalyst activity. Whereas this particular iron catalyst was inactive at 225° C it becomes quite active above 265° C. Table IV shows the effect of on-stream time on catalyst 26. Activity appears to drop quite rapidly with time and after 10 hours was almost nil; however, raising the temperature to 250° C restored the catalyst to moderate activity. Treating the catalyst with H₂ at 450° C restores the catalyst to near its previous activity. The cause of activity loss while on stream and its restoration are not understood at present but this may have to do with blocking of the catalyst surface by high molecular substances which are produced in small amounts but which do not leave the catalyst surface at the temperature of reaction. This is the subject of further investigation.

Cobalt Catalyst

Catalyst 33 is a cobalt on γ -alumina catalyst prepared by coprecipitation of cobalt and aluminum nitrates with sodium carbonate. This catalyst had low activity compared with iron but could be brought up to appreciable activity by raising the temperature to 250° C. At this condition, this catalyst showed high methane and C₂ production with no alcohol formation. Still the activity for C₂-C₄ production was considerable and these products were better than 40% unsaturated. These results make cobalt an interesting metal for additional study.

Copper Catalyst

Catalyst 34 is copper supported on γ -alumina prepared in the same manner as the cobalt catalyst. Copper has low activity and the principle product is R-OH, mostly methanol. This was as expected and it was also expected that copper would show CO₂ formation since it is an important component of low temperature water gas shift catalysts (15). Even though water was there as a product, copper showed no CO₂ formation. This is an interesting finding and should be studied further.

Nickel Catalyst

Catalyst K6 is a γ -alumina supported nickel catalyst prepared by precipitation as with previous copper and cobalt catalysts. This particular catalyst formulation contained copper as well. It is well known that nickel is an excellent methanation catalyst. Consequently, we have not yet examined nickel by itself in our treating program. Copper was found to alter the catalytic properties of cobalt in a favorable way for our purposes so a corresponding catalyst of nickel-copper was investigated. The data in Table II show this catalyst to have low activity requiring 275° C to show 18% conversion of the CO. Carbon dioxide formation indicates strong water gas shift tendency. Copper does not appear to be present as copper metal since no alcohol was formed.

Cobalt-Thoria

This catalyst K1 was prepared by a method given in the literature (16). Cobalt and thorium as nitrates were coprecipitated with ammonium carbonate solution and to the resulting slurry Kieselguhr was added. This mixture was then dried and pelleted. It was found to be highly active and produced high yields of paraffins particularly CH₄ and C₅-C₃₀ long chain hydrocarbons. The C₂-C₄ hydrocarbons were mostly saturated. This was expected based on data in the literature (16).

Ruthenium Catalyst

A catalyst based on this metal has not yet been tested. Literature data indicate that such a catalyst is likely to yield CH₄ and C₅ high molecular weight paraffins. It will, however, be tested under our conditions and reported later.

CONCLUSIONS

Catalysts based on iron and cobalt appear to have the most potential for synthesizing C₂-C₄ hydrocarbons. Future work will be concentrated on improving the selectivity and stability of iron catalysts. Additional effort is also indicated for cobalt and possibly nickel to improve selectivity. Some work is also planned on the mechanism of CO₂ production.

The water gas shift appears to be an important reaction between CO feed and water produced in the reaction. Additional effort is indicated to determine the activity of our catalysts for this reaction, and the role this reaction plays in our synthesis. Other types of catalytic metals and different supports will also be investigated in future work.

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TABLE I
Composition and Treatment of Catalysts Studied

Wt-pct (f)	ICI	22	23	26	33	34	K6	K1
Fe ₃ O ₄	1/ 94.0	2/ --	2/ --	2/ --	3/--	3/ --	4/ --	4/ --
Fe	--	79.3	52.2	59.4	--	--	--	--
Cu	--	19.7	--	29.3	--	18.4	12.8	--
Co	--	--	3.9	--	14.7	--	--	49.2
Ni	--	--	--	--	--	--	13.7	--
CaO	2.0	--	--	5.9	--	--	--	--
MgO	0.3	--	--	0.9	--	--	--	--
Al ₂ O ₃	2.5	--	--	3.7	85.3	81.6	73.5	--
SiO ₂	0.4	--	--	--	--	--	--	--
K ₂ O	0.8	1.0	1.0	0.8	--	--	--	--
Kieselguhr	--	--	42.9	--	--	--	--	43.1
ThO ₂	--	--	--	--	--	--	--	7.7

1/ Pretreatment a, e, b

2/ Pretreatment a, e

3/ Pretreatment c

4/ Pretreatment d

a Reduced in H₂ at 550⁰ C for 20 hr; then nitrided in NH₃ for 6 hr

b Reduced in H₂ at 450⁰ C for 20 hr

c Reduced in H₂ at 500⁰ C for 4 h4.

d Calcined in air at 520⁰ C for 4 hr, then reduced in H₂ at 275⁰ C for 4 hr

e Regenerated in H₂ at 500⁰ C for 20 hr

f Compositions of catalysts are based on the calculated quantities of each metal salt taken for preparation.

TABLE II

Operating data on catalysts tested

Catalyst	Fe 23	Fe 22	Fe 26	Fe IC1	Co 33	Cu 34	Co ₂ O ₃ K1	Cu ₂ O K2	Cu ₂ Ni K6
Pretreatment*	a	a	a	a	b	b	c	c	c
Temp, C	225	225	260	225	250	275	225	225	275
Pressure, psig	750	750	750	750	750	750	120	120	750
Space velocity, cc/gm/sec	1.54	1.54	1.54	1.54	0.77	0.77	0.6	0.6	0.77
H ₂ /CO	1/1	1/1	1/1	2/1	2/1	2/1	7/3	7/3	7/3
CO conversion, %	57.6	0.9	94.7	89.4	16.96	11.57	84.0	84.0	18.3
Product selectivity, %									
CO ₂	51.6	0.0	64.7	39.4	5.3	0.0	7.0	7.0	63.1
CH ₄	15.8	25.9	8.3	11.7	34.0	11.6	32.0	32.0	24.4
C ₂ -C ₄	18.7	51.6	17.5	24.8	27.4	5.3	12.0	12.0	9.7
C ₅ ⁺	10.3	22.5	8.7	22.0	33.3	1.2	49.0	49.0	2.8
R-OH	3.6	0.0	0.8	2.1	0.0	81.9	--	--	0.0
O/P	2.0	2.2	1.3	2.9	0.77	0.44	0.14	0.14	0.06
Pretreatment*									
a	Reduced in H ₂ at 550° C for 20 hr nitrided in NH ₃ , 325° C for 6 hr								
b	Reduced in H ₂ at 520° C for 4 hr								
c	Calcd in air-520° C for 2 hr reduced in H ₂ at 275° C for 4 hr.								

TABLE III
Effect of pretreatment and temperature of reaction for commercial
iron catalyst

	ICI-35-4		22		
	a	b	a	a	a
Pretreatment					
Temp, ° C	225	250	225	265	250
Pressure, psig	750	750	750	750	750
Space velocity, cc/gm/sec	1.54	1.54	1.54	0.77	0.77
H ₂ /CO	2/1	1/1	1/1	1/1	1/1
CO conversion, %	89.4	75.9	0.9	47.7	20.7
Product selectivity, %					
CO ₂	39.4	57.9	0.0	54.3	50.0
CH ₄	11.7	2.5	25.9	8.5	8.1
C ₂ C ₄	24.8	21.5	51.6	22.2	23.1
C ₅ ⁺	22.0	18.1	22.5	12.1	17.3
R-OH	2.1	0.0	0	2.9	1.5
O/P	2.90	4.65	2.2	1.62	1.5

a Reduced in H₂ 550⁰ C, for 20 hr, nitrided in NH₃, 325⁰ C for 6 hr

b Reduced in H₂ at 450⁰ C for 20 hr

TABLE IV
Effect of On-Stream Time and Regenerability of Iron Catalyst

Catalyst	Fresh 26*			Regenerated with H ₂ at at 450° C. for 20 ² hr
	0.5	5.0	6.0	
Hr on stream	0.5	5.0	6.0	21**
Temp, ° C	260	220	220	225
Pressure, psig	750	750	750	750
Space velocity, cc/gm/sec	1.54	1.54	1.54	1.54
H ₂ /CO	1/1	1/1	1/1	1/1
CO conversion, %	94.7	54.9	35.6	38.3
Product selectivity, %				
CO ₂	64.7	46.0	45.3	39.3
CH ₄	8.3	11.5	9.1	4.9
C ₂ C ₄	17.5	19.0	18.4	15.7
C ₅ ⁺	8.7	22.3	25.9	31.8
R-OH	0.8	1.2	1.3	8.3
O/P	1.24	3.33	3.81	3.63
				2.8
				2.8
				0.2
				18.6
				17.7
				10.9
				52.8
				44.8
				5.0
				20.7
				29.3
				0.2
				3.8

* Reduced in H₂ at 550° C 20 hr, nitrified in NH₃ for 6 hr (#26).

** Catalyst run discontinued at 10 hr left standing at 220° C in helium overnight; at hr 21 in the cycle the temperature was increased to 250° C

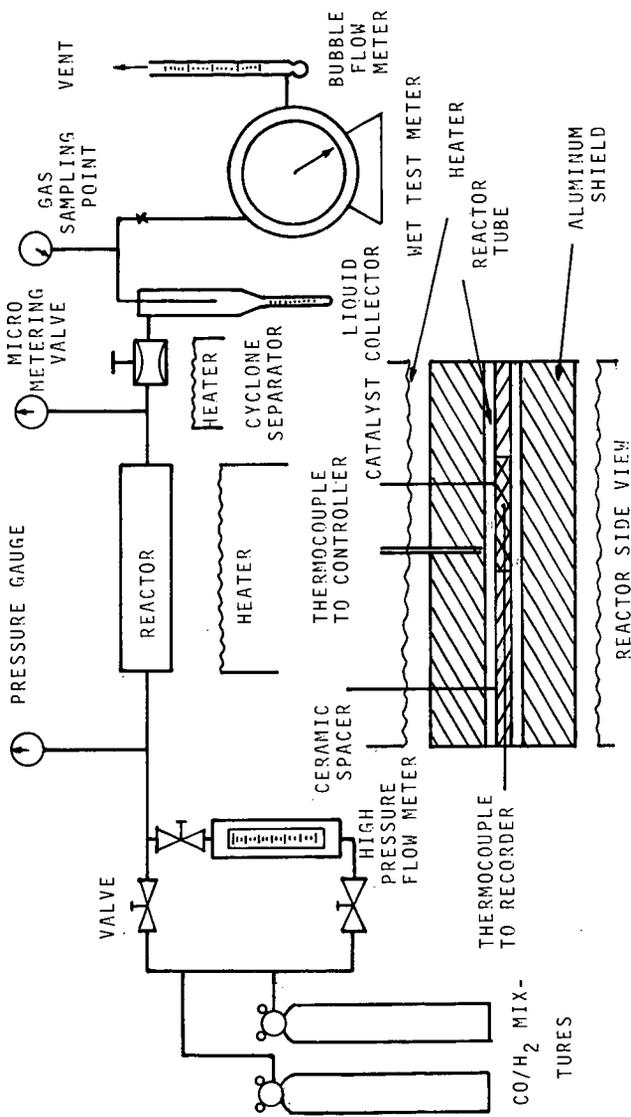


FIGURE I.- Reaction System Flow Diagram and Reactor Side View