

## Fischer-Tropsch Reaction Studies with Supported Ruthenium Catalysts

### I. Product Distributions at Moderate Pressures and Catalyst Deactivation

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Hydrocarbon synthesis especially in the range C<sub>5</sub>-C<sub>12</sub> using 0.5% ruthenium-on-alumina pellets at elevated pressures (8 to 16 bar) was undertaken. For this purpose a stirred gas-solid reactor was used together with a gas chromatograph fitted with an on-line hot sampling valve for a complete product analysis up to C<sub>12</sub>. Product spectra consisting mainly of saturated hydrocarbons and with C<sub>5</sub>-C<sub>12</sub> fractions of the order of 23.3-26.9 mol% (of total hydrocarbons) or 54.0-59.5 wt% (assuming saturated hydrocarbons only) were obtained at temperatures close to 500 K. At 550 K and higher, there appears to be a critical space velocity for an optimum yield of C<sub>5</sub>-C<sub>12</sub>. The selectivity of the hydrocarbons leaving the reactor was found to be influenced by the partial pressure of the carbon monoxide inside the reactor. Some catalyst characterizations are also presented, such as carbon burn-off and BET areas, obtained from samples taken at instants when product analyses were performed.

#### INTRODUCTION

Ruthenium-on-alumina catalyst without any promoters and containing as little as 0.5% Ru has been known for many years to be an effective catalyst in hydrocarbon synthesis (1-4). The composition of the products, which may include gases, liquids, and waxes at room temperature, can vary substantially over moderate ranges of temperatures (473-598 K) and pressures (1-20 bar) (3, 5). Among the Group VIII metals Fe, Ni, Co, Ru, Rh, Pd, Pt and Ir, Vannice (5) showed that ruthenium produces a spectrum with the highest average molecular weight and the largest C<sub>5</sub><sup>+</sup> fraction, even at atmospheric pressure.

Despite the fact that the Fischer-Tropsch reaction over Fe, Co, and Ru has been a subject of so much research for

many years, no thorough quantitative investigations concerning any of the higher molecular weight hydrocarbons exist in the literature. Most kinetic studies have been confined to reaction rates based upon the consumption of H<sub>2</sub> + CO (3, 6-8), the consumption of CO (9, 10) and the formation of methane (11-13) over "undefined" catalyst surfaces. Rate data over well-characterized catalyst surfaces have only recently been published. Such investigations include those by Vannice (5, 14), who considered the rate of formation of methane and Dalla Betta *et al.* (15) who considered the initial rate of formation of total hydrocarbons in addition to the rate of methane formation.

The formation of carbonaceous deposits on the catalyst surface (10, 15) and possible volatile carbonyl formation (2) over very long periods, thus causing deactivation,

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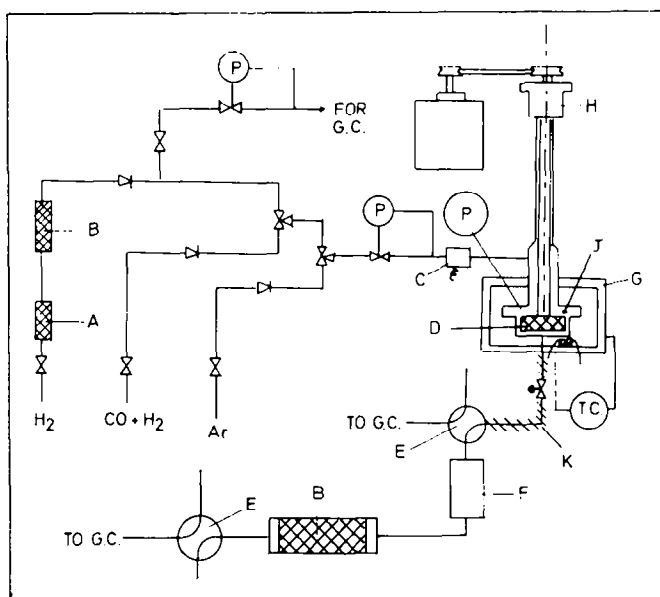


FIG. 1. Experimental apparatus: A, Englehard De-oxo; B, 5A molecular sieve; C, Matheson flow meter; D, catalyst basket; E, sampling valve; F, water trap; G, temperature-controlled oven; H, magnetic drive; J, thermocouple; K, heated line.

normally accompany the synthesis reaction under conditions favorable for the formation of hydrocarbons above  $C_2$ . The extent of this overall activity loss will depend on the catalyst, the  $H_2/CO$  ratio, the temperature, and the total pressure.

For the determination of accurate and unambiguous kinetic data for highly exothermic reactions, most investigators have hitherto used differential reactors, thus minimizing heat and mass transfer limitations by virtue of the low conversions obtained (5). These limitations may however also be overcome by using a stirred gas-solid reactor (SGSR) as originally developed by Carberry (16) and further developed by Brisk *et al.* (17) and also used by Tajbl *et al.* (18) for their methanation studies.

This investigation was undertaken in order to evaluate quantitatively the catalytic activity of 0.5% ruthenium-on-alumina with respect to liquid hydrocarbon formation and to identify and characterize the accompanying deactivation. This par-

ticular paper presents an examination of the product spectra and selectivities obtained under isothermal, moderate pressure, and perfectly mixed conditions characteristic of the SGSR, together with some partially deactivated state characterizations. Subsequent papers in this series will present more characterizations and kinetic data.

## EXPERIMENTAL

### Apparatus

The apparatus used in this investigation is shown schematically in Fig. 1. Hydrogen, synthesis gas ( $H_2/CO$ ), and argon were drawn off pressurized cylinders by operation of two three-way valves. After leaving the three-way valves the gas passed into a M-600 pressure regulator which was preset to produce the reactor operating pressure required. This system enabled the reactor to be operated at a fixed pressure over a range of flow rates into the reactor and over a range of conversions. The flow rate

of gas into the reactor was adjusted indirectly by means of a stainless-steel needle valve on the outlet of the reactor, and the flow rate was measured by means of a Matheson Model 8116-0252 mass flow meter.

The reactor employed was in ICI-developed stirred gas-solid reactor (SGSR) Mark VI, which has been described by Brisk *et al.* (17). This reactor had good mixing characteristics for the range of flow rates between 25 and 415 ml/min and stirrer speeds above 3000 rpm as used in this investigation. This was confirmed by standard pulse tests similar to that described by Tajbl *et al.* (18) and is also in agreement with data supplied by Brisk *et al.* (17). Gas entered the reaction vessel through a feed line above the catalyst basket, and the reactor outlet was at the bottom of the reactor pot below the catalyst basket. This resulted in a net downward flow of gas away from the bearing surfaces, thus preventing accumulation of catalyst fines and/or reaction products in the bearing areas. The catalyst basket used was a cruciform shape which had a total charge volume of 10.4 cm<sup>3</sup>. Heating of the reactor was achieved by a Perkin-Elmer F100 gas chromatograph oven, and the temperature was controlled within  $\pm 1$  K. Temperatures inside the reactor were measured with a Fluke Model 2100A digital thermometer together with a Pyrotex Chromel-Alumel thermocouple. The reactor vessel and tubing were made of stainless steel, and the reactor gaskets were annealed copper rings.

Analysis of the product streams from the reactor was by gas chromatography with hydrogen as a carrier gas. Because of the complexity of the product stream, which contained water vapor and condensable hydrocarbons together with unconverted hydrogen and carbon monoxide, a direct measurement of product stream flow rate was not possible. A system consisting of two separate gas chromatographs (G.C.) was thus devised in order to accomplish this.

The one G.C. measured the complete product spectrum and the other measured only the CH<sub>4</sub>, CO, and C<sub>2</sub>'s (which was normally very low) after the removal of water and hydrocarbons above C<sub>2</sub>'s. These analyses, together with a measure of the flow rate of the final effluent stream (CH<sub>4</sub>, CO, C<sub>2</sub>, and H<sub>2</sub>) yielded the flow rate of the total product stream directly from the reactor. The chromatographs used were a Varian 2800 having dual columns of Chromosorb 102 and T.C.D. operated with temperature programming, and a Beckman G.C. 2A single column T.C.D. operated isothermally. Gas sampling was in both cases by sampling valves, the sample for Varian analysis being taken by a Carle sampling valve enclosed in a heated Beckman G.C. 4 oven at 473 K while the sample for analysis on the Beckman G.C. was taken by a Beckman valve operated at ambient temperature. The product stream from the reactor passed through an electrically heated copper-jacketed stainless-steel line to the heated Carle sample valve. From the heated sample valve the product stream passed firstly through a cold trap to remove water and higher hydrocarbons and then through a silica gel drier and 5A molecular sieve column before passing through the second sample valve. The flow rate of this stream was measured by means of a bubble flow meter under ambient conditions.

#### *Experimental Procedure*

Each experiment utilized a fresh charge of catalyst taken from the same container obtained from the supplier. This charge was reduced for 12 hr with flowing hydrogen at a rate of 10 ml/min at a temperature of 673 K. After switching over to the synthesis gas for reaction, samples of the product stream were analyzed periodically in order to establish essentially the deactivation within the reactor. The selectivities of the hydrocarbons (considering the total hy-

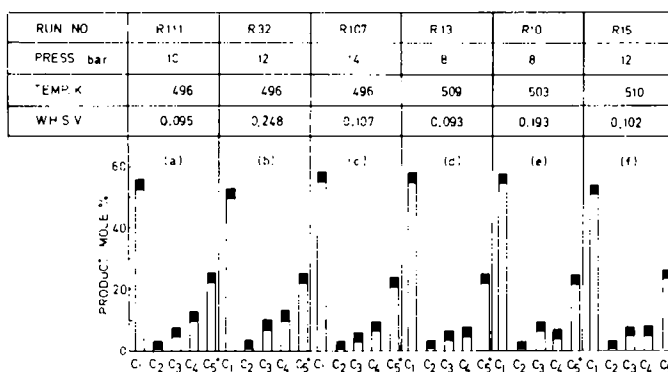


FIG. 2. Product distributions at 496 K and 503-510 K.

drocarbon fraction only) were found to be practically the same over both the initial rapid deactivation period and a subsequent slow deactivation period. The product distributions and selectivities reported in this investigation were obtained from analysis of samples taken at a time when the deactivation rate was very small, which was usually at about 2 hr after the start of the experiment. At this instant, the reactor outlet valve was closed, and the system was depressurized, blanketed with argon, and cooled. The catalyst charge was then analyzed for carbon by a gasometric method using a "Leco" apparatus, and its BET area was determined by conventional nitrogen adsorption (19).

During the course of this investigation, the following ranges of operating variables

were covered: temperature from 473-573 K; total pressure from 8 to 16 bar; feed ratio of 3:1 (H<sub>2</sub>/CO); and total flow rate from 25 to 415 ml/min measured at NT

*Materials Used*

The catalyst used in this study was commercial preparation of nominally 0.5 (weight) ruthenium on  $\gamma$ -alumina from Engelhard Industries, Inc. The catalyst was in the form of approximately 3 × 3-mm cylindrical pellets with the ruthenium impregnated only on the outer shell of the pellet. This outer shell was estimated, by electron microprobe analysis, to be approximately 300  $\mu$ m with an average maximum concentration of 3.0% at 10  $\mu$ m from the edge.

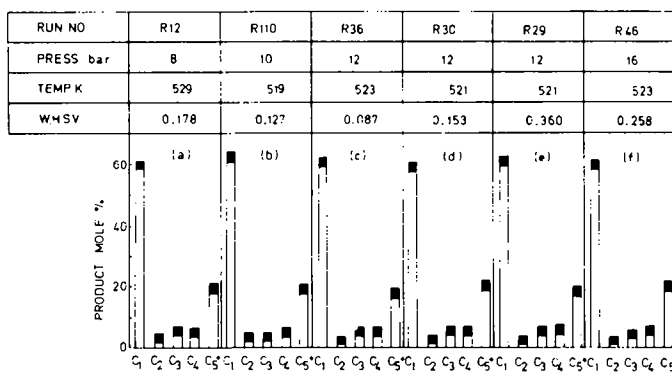


FIG. 3. Product distributions at 521-529 K.

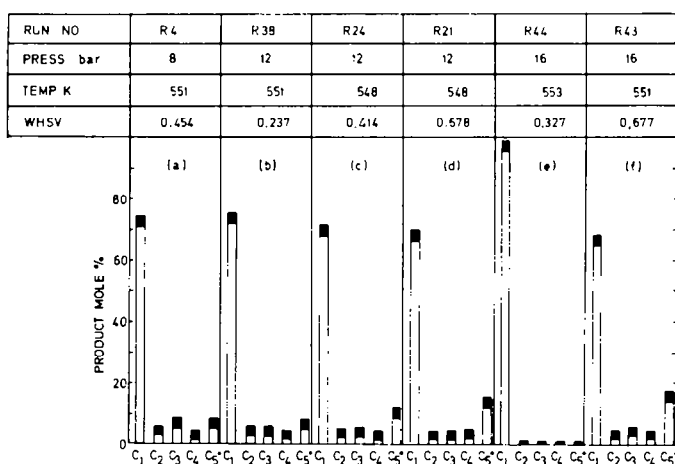


Fig. 4. Product distributions at 548-553 K.

Reducing hydrogen was Matheson U.H.P. grade and before use was passed through an Engelhard De-oxo unit and a 5A molecular sieve drier. The synthesis gas was premixed by the suppliers from Matheson C.P. grade carbon monoxide and Matheson U.H.P. hydrogen.

## RESULTS AND DISCUSSION

### Product Distributions

The product distributions obtained over different batches (about 5.5 g) of catalysts are shown in Figs. 2-5 as a function of tem-

perature, pressure, and space velocities (mass flow rate per hour per mass of total catalyst). The products are represented as the number of C atoms per molecule, and concentrations are plotted as mole percents of total hydrocarbons. The separation of the different carbon number fractions was easily achieved with the column and temperature programmer described above, and the different fractions appeared to consist essentially of saturated hydrocarbons with very small amounts of olefins similar to that obtained by Pichler *et al.* (20) also with ruthenium. A further analysis

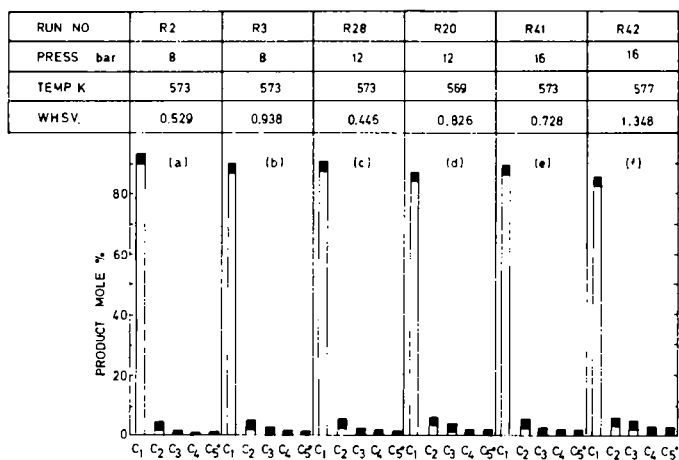


Fig. 5. Product distributions at 569-577 K.

TABLE 1

Distribution of C<sub>5</sub> to C<sub>12</sub> (Mole Percent of Total HC), CO Conversion (Mole Percent), and Concentrations of CO<sub>2</sub> and H<sub>2</sub>O (Mole Percent of Exit Stream)

Run no.	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>5</sub> <sup>+</sup>	CO conversion	CO <sub>2</sub>	H <sub>2</sub> O
R111	8.07	6.34	4.04	3.75	1.73	1.15	—	—	25.07	13	0.087	2.84
R32	5.79	6.05	4.53	3.78	3.53	1.01	—	—	24.69	6	0.018	0.98
R107	7.10	5.83	5.07	3.30	2.03	—	—	—	23.33	16	0.138	3.07
R13	6.21	5.86	4.35	3.10	2.48	1.86	0.83	—	24.69	19	0.070	4.06
R10	5.27	4.81	4.18	4.65	1.86	1.50	—	—	23.27	9	0.030	1.85
R15	7.42	6.28	4.28	3.94	3.42	1.54	—	—	26.87	23	0.190	5.04
R12	5.08	4.39	3.69	2.61	1.94	1.94	1.14	0.95	21.74	57	0.200	17.10
R110	5.44	4.49	3.84	2.60	2.01	1.31	0.85	—	20.53	46	0.290	11.45
R36	5.29	4.29	3.19	2.49	1.66	1.25	0.97	0.35	19.48	39	0.198	10.80
R30	5.24	4.44	3.46	3.11	2.66	2.31	0.98	0.35	22.54	37	0.156	9.22
R29	5.55	4.36	3.56	2.38	1.98	1.19	0.99	—	20.00	15	0.055	3.82
R46	5.27	4.28	4.28	2.97	2.14	1.66	0.95	0.48	22.03	27	0.140	6.66

of a condensate directly from the reactor by mass spectrometry also indicated the presence of mainly saturated hydrocarbons with trace amounts of alcohols. The separation of the branched isomers within a carbon number group was, however, not considered in this investigation.

A further breakdown of the C<sub>5</sub><sup>+</sup> fractions as shown in Figs. 2-5 is shown in Tables 1 and 2 together with the amounts of carbon dioxide and water formed and the mole percent conversion of carbon monoxide.

For the ranges of reaction conditions examined, namely, 473-573 K, 8-16 bar, and weight hourly space velocities (WHSV) of 0.087-1.348 hr<sup>-1</sup>, the methane content in the total hydrocarbon fraction was extremely sensitive to temperature as previously observed (2, 18), and to a certain extent dependent on space velocities and pressure at high temperatures. The methane content varied from nearly 100 mol% at high temperatures and low space velocities (see R44 in Fig. 4e) to 54.30 mol% at low temperatures and high space velocities (see R32 in Fig. 2b) or nearly 100 and 19.9 wt%, respectively. The weight analysis was based on the assumption of production of alkanes only. It should be noted here that the upper limit of the space velocity for a

particular set of temperature and pressure conditions was chosen such that the measurable product spectrum did not exceed C<sub>12</sub>. This procedure was adopted because interest was confined to products corresponding in boiling range to a suitable gasoline fraction which was completely gaseous at a reasonably low working temperature, for example 473 K, this being the lowest reactor temperature used. The C<sub>5</sub><sup>+</sup> fraction on the other hand can be as high as 26.9 mol% or 59.6 wt% (see R15 in Fig. 2f) at 510 K and 12 bar as compared to about 17 mol% at 483 K and 1 bar in a differential reactor with Ru catalyst by Vannice (5), and 33.4 wt% (C<sub>5</sub>-C<sub>11</sub>) at 593-613 K and 22 bar with the Industrial Synthol reactor with iron catalysts, as reported by Frohning and Cornils (21). The latter spectrum, however, contained a very high (70%) proportion of olefins and also produced hydrocarbons up to C<sub>20</sub>, with the C<sub>12</sub>-C<sub>20</sub> fraction being about 5.1 wt% together with a fair amount of alcohols, ketones, and acids (8.8 wt%).

It is interesting to note that the maximum hydrocarbon yield other than C<sub>1</sub> occurs over the range C<sub>4</sub>-C<sub>5</sub> (mole percent) or C<sub>4</sub>-C<sub>7</sub> (weight percent) for 480-530 K, whereas for temperatures of 550 K and

TABLE 2  
Distribution of C<sub>5</sub> to C<sub>12</sub> (Mole Percent of Total HC), CO Conversion (Mole Percent),  
and Concentrations of CO<sub>2</sub> and H<sub>2</sub>O (Mole Percent of Exit Stream)

Run no.	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>5</sub> <sup>+</sup>	CO conversion	CO <sub>2</sub>	H <sub>2</sub> O
R4	3.09	2.02	1.15	0.84	0.52	0.31	—	—	7.94	39	0.090	10.08
R38	3.12	2.14	1.16	0.78	0.49	0.17	0.11	—	7.97	70	0.820	24.58
R24	4.04	2.99	2.17	1.30	0.68	0.34	0.29	—	11.81	41	0.132	12.17
R21	4.24	3.60	2.40	1.84	1.15	0.71	0.57	—	14.50	34	0.080	9.37
R44									0.00	96	0.981	40.96
R43	4.03	3.35	2.77	2.42	1.68	1.58	0.59	0.20	16.63	46	0.135	6.80
R2	0.28	0.10	0.04	—	—	—	—	—	0.43	72	0.400	22.68
R3	0.59	0.22	0.08	—	—	—	—	—	0.89	47	0.140	12.85
R28	0.67	0.28	0.12	—	—	—	—	—	1.05	77	0.537	27.38
R20	1.20	0.47	0.14	—	—	—	—	—	1.81	41	0.110	11.12
R41	0.72	0.31	0.17	0.16	—	—	—	—	1.36	74	0.491	27.43
R42	1.34	0.76	0.34	0.11	—	—	—	—	2.55	45	0.153	14.07

above maxima occur at C<sub>2</sub>-C<sub>3</sub> (mole or weight percent). Other spectra reported by Vannice (5) with ruthenium at 1 bar and 483 K (with H<sub>2</sub>/CO 3:1) have a maxima at C<sub>3</sub> (mole percent). The results of Frohning and Cornils (21) on the Synthol reactor appear to display a maximum at C<sub>3</sub> (16.2 wt%) despite the presence of a fair amount of very high molecular weight hydrocarbons. Cobalt on a weight basis gives a maximum at C<sub>5</sub> with a yield of about 36-46 wt% C<sub>5</sub>-C<sub>12</sub> over a range of pressures, as reported by Storch *et al.* (22).

Tajbl *et al.* (18) examined methanation in a reactor similar to that used in this investigation and found that over a rather limited range of low space velocities the

higher hydrocarbons yields were very low over ruthenium and iron catalysts. They attributed this to hydrogenolysis especially at a high hydrogen:carbon monoxide ratio and a high total pressure. The results presented in Figs. 4 and 5 and Table 2 show the effect of a range of space velocities at 12 bar (R38, R24, R21; and R28, R20) and 16 bar (R44, R43; and R41, R42) at 548-553 and 569-577 K, respectively, on the product spectrum and CO conversion. This effect is more marked at 548-553 K because of a fair yield of higher hydrocarbons. With increasing space velocities conversions decrease, methane content decreases, and C<sub>5</sub><sup>+</sup> fraction increases. The methane and C<sub>5</sub><sup>+</sup> fractions produced at

TABLE 3  
C<sub>2</sub> Selectivity with Respect to Methane<sup>a</sup>

	Catalyst	Pressure (bar)	Temperature (K)	C <sub>2</sub> /C <sub>1</sub> (mole ratio)	C <sub>2</sub> /C <sub>1</sub> (weight ratio)
This investigation	Ru	8-16	481-603	0.079 (max) (R38)	<0.132
Vannice (5)	Ru	1	483	0.145	0.258
Vannice (5)	Fe	1	513	0.281	0.468
Frohning and Cornils (20) (Synthol)	Fe	22	593-613	—	0.779

<sup>a</sup> Feed gas: H<sub>2</sub>/CO, 3:1.

TABLE 4  
Effect of Pressure at Approximately  
Constant Conversions

Temperature (K)	Pressure (bar)	Conversion (CO mol%)	C <sub>5</sub> <sup>+</sup> (wt%)	C <sub>1</sub> (wt%)
551	8	39	26.77	44.09
548	12	41	38.40	39.08
551	16	46	48.90	31.44
573	8	72	1.90	84.92
573	12	77	4.66	78.37
573	16	75	6.04	74.75
573	8	47	3.75	78.15
569	12	41	7.15	70.78
577	16	46	10.08	66.17

±525 and ±500 K appear to be largely independent of space velocity (and consequently conversion) at conversions less than 60%. Thus as the contact time of the product with the catalyst increases, at ±550 K and higher, so the higher hydrocarbon content decreases forming more methane, with a higher CO conversion. This condition corresponds to catalyst with a very low CO surface coverage which is known to favor hydrogenolysis of the higher hydrocarbons (23, 24). The inhibit-

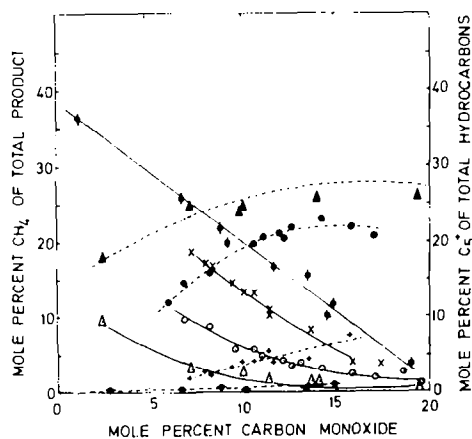


Fig. 6. Methane and C<sub>5</sub><sup>+</sup> selectivities at 8 bar: ●, ●, ±573 K; ×, +, ±548 K; ○, ●, ±523 K; △, ▲, ±498 K; —, methane; ----, C<sub>5</sub><sup>+</sup>.

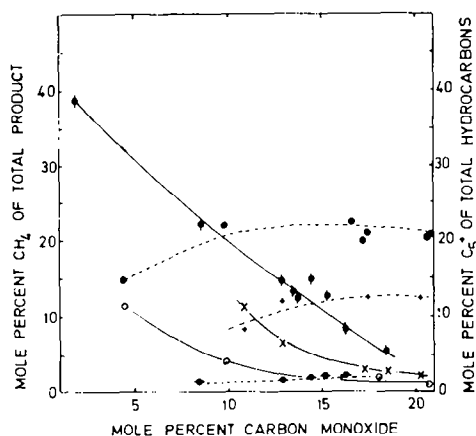


Fig. 7. Methane and C<sub>5</sub><sup>+</sup> selectivities at 12 bar: ●, ●, 573 K; ×, +, 548 K; ○, ●, 523 K; —, methane; ----, C<sub>5</sub><sup>+</sup>.

ing effect of a high surface coverage of CO on hydrocarbon hydrogenolysis to methane was well demonstrated by Dalla Betta *et al.* (15). Therefore at these temperatures it appears that space velocity is an extremely sensitive parameter and would require precise control for an optimum production of higher hydrocarbons. At lower temperatures, however, space velocity has a significant effect on the CO conversion only, and consequently on the total contribution to the product by the individual hydrocarbons.

The C<sub>2</sub> yields corresponding to high C<sub>5</sub><sup>+</sup> yields with ruthenium catalysts are distinctly lower than obtained with iron catalysts as shown in Table 3. The hydrogen:carbon monoxide ratios for all the experiments reported were high inside the reactor, and this according to Tajbl *et al.* (18) also favors hydrogenolysis, thus it is presumed that the hydrogenolysis of the higher hydrocarbons to mainly methane is responsible for the low C<sub>2</sub> yields (23, 24). The effect of pressure on the product distributions can best be appreciated when experiments with approximately the same conversions are compared at a particular temperature, as shown in Table 4. High pressures clearly favor C<sub>5</sub><sup>+</sup> fractions which correspond to higher absolute rates per unit



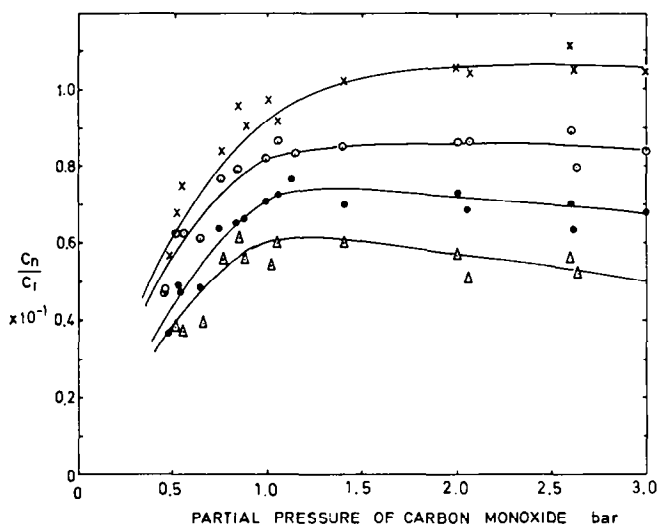


FIG. 8.  $C_4$  to  $C_7$  selectivities at  $\pm 528$  K:  $\times$ ,  $C_4$ ;  $\circ$ ,  $C_6$ ;  $\bullet$ ,  $C_6^+$ ;  $\Delta$ ,  $C_7$ .

weight of catalyst, and which is also in agreement with Karn *et al.* (3) who examined different  $H_2/CO$  ratios at 21.4 bar.

### Selectivities

The influence of carbon monoxide on selectivity was found to be most dominant in this investigation, as shown in Figs. 6-9. The selectivities of methane and  $C_5^+$  fraction at 8 and 12 bar as a function of carbon monoxide concentration (mol%) are shown,

respectively, in Figs. 6 and 7 at four different temperatures. The  $C_5^+$  selectivity at high carbon monoxide concentrations was found to be approximately constant over the pressure range 12 to 16 bar, especially at the low temperatures.

Figures 8 and 9 show the ratios of the moles of hydrocarbons formed,  $C_4$ ,  $C_6$ ,  $C_6^+$ , and  $C_7$ , to the moles of methane formed as a function of the partial pressure of carbon monoxide. These results are confined to  $\pm 525$  and  $\pm 550$  K, respectively, for all

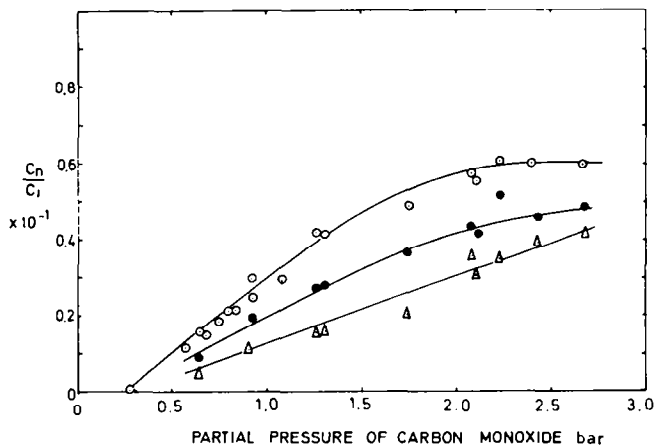


FIG. 9.  $C_5$  to  $C_7$  selectivities at  $\pm 548$  K:  $\circ$ ,  $C_5$ ;  $\bullet$ ,  $C_6$ ;  $\Delta$ ,  $C_7$ .

TABLE 5  
 Catalyst Properties

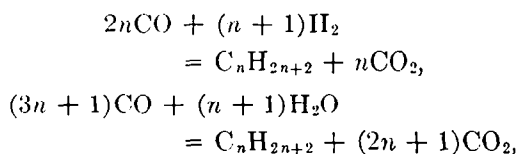
Run no.	Reaction conditions		Rate of CH <sub>4</sub> formation [(g mol) <sup>-1</sup> min <sup>-1</sup> (g of Ru) <sup>-1</sup> × 10 <sup>-3</sup> ]			Final C <sub>5</sub> <sup>+</sup> (mol%)	Carbon burnoff (wt%)	BET area (m <sup>2</sup> g <sup>-1</sup> )
	(K)	(bar)	@±	@±	Final <sup>a</sup>			
			50 min	100 min				
R6	551	8	14.88	13.30	12.98	5.825	0.26	168.9
R13	509	8	1.02	0.68	0.42	24.690	5.20	139.8
R108	575	10	—	51.04	48.42	2.263	0.10	212.8
R110	519	10	7.56	2.30	1.93	20.529	3.54	155.6
R22	600	12	69.64	69.46	69.46	0.000	0.05	203.5
R36	523	12	—	1.70	1.26	19.483	3.30	134.7
R103	573	14	70.24	62.28	56.25	1.113	0.16	200.2
R107	496	14	3.26	0.73	0.52	23.331	4.48	120.6
R41	573	16	66.08	54.17	51.12	1.371	0.07	160.0
R45	523	16	3.34	2.71	2.20	17.462	1.14	139.1
Fresh catalyst	—	—	—	—	—	—	0.00	272.7

<sup>a</sup> When sample was taken for complete analysis.

experiments performed, namely from 8 to 16 bar and with CO conversions as low as 5%. This ratio is also the rate of formation of the respective hydrocarbons relative to methane. These figures show a positive dependence below a certain critical partial pressure of carbon monoxide which decreases with a decrease in temperature. In some cases, especially at low temperature, there is a slight negative dependence of this ratio for the higher hydrocarbons above this critical CO partial pressure. This critical carbon monoxide partial pressure appears to give the most favorable surface condition for C<sub>5</sub><sup>+</sup> formation. This condition can be achieved at any total pressure, but this will no doubt correspond to a very low CO conversion at a low pressure. It should be noted, however, that this result has been derived from experiments in which the total molar concentration of C<sub>5</sub><sup>+</sup> is small relative to all the other components in the product.

From a comparison of Figs. 8 and 9 it is clear that at high temperatures a much

greater partial pressure would be required in order to reach the optimum. Dry (10) noted that the partial pressure of CO<sub>2</sub> and not the H<sub>2</sub>/CO ratio was dominant for fluidized bed operation at high temperatures, whereas for fixed-bed wax-producing reactors the H<sub>2</sub>/CO ratio was dominant with the partial pressure of CO<sub>2</sub> of no importance. In this investigation, however, the CO<sub>2</sub> concentration in the product was very small as shown in Tables 1 and 2. This feature of ruthenium catalysts was also observed by Shultz *et al.* (4) at the same H<sub>2</sub>/CO feed gas, namely 3:1. This result indicates that the extents of the reactions involving CO<sub>2</sub> production such as:



are indeed very small over ruthenium metal in comparison to other synthesis reactions. McKee (11) examined the effect of carbon

monoxide on the activity of ruthenium catalysts relative to hydrocarbon synthesis and found that the presence of carbon monoxide actually enhances simultaneous hydrogen adsorption thus producing surface coverages favorable for reaction. This property will no doubt depend on the partial pressure of the carbon monoxide which is in equilibrium with the catalyst surface.

### *Catalyst Deactivation*

Table 5 shows how the rate of methane formation per unit weight of catalyst changes with time during experiments, which were started with fresh catalyst after a period of reduction with ultrapure hydrogen. These changes are considered to be caused by the hydrodynamic and thermal response of the reactor and by catalyst deactivation. The former two effects would certainly be confined to the initial start-up period which was estimated to be of the order of 15 min by pulse and temperature measurements.

The amount of carbonaceous material present on the catalysts and the BET areas at instants when the reactions were terminated are shown in Table 5.

The weight percent of carbonaceous material is the highest for experiments performed at low temperatures favoring  $C_6^+$  formation and at which the change in rate of methane formation is the highest, relative to the initial rate (zero time) corresponding to a "clean" catalyst activity. It should be noted that deactivation always occurred; that is, steady-state operation was never attained. The exact nature of the carbonaceous material is not known, but presumably it is elemental carbon and/or some high molecular weight hydrocarbon deposit (wax). This, however, needs further examination since the regeneration of the catalyst would certainly be necessary in order to make ruthenium competitive economically with iron on an industrial scale. The BET area of the catalyst also

changed markedly and in some cases was as low as 40% of its original value.

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