3.5.2 Experiments Performed

Before discussing the complete run, let us list the experiments in the order that they were performed (Table 3.35). After each experiment, the catalyst was kept overnight in flowing He at the same temperature and pressure used in the experiment. The following table gives the experimental conditions and duration of each test:

Table 3.35

Experimental Conditions[1] for Run 7

Experiment[2]	H_2/CO	SV, V/V/h	T, °C	P, kPA	Time, h
7-1	1.97	200	350	2000	4.9
7-2	1.94	200	400	2000	4.1
7-3	2.02	200	450	2000	3.7
7-4	1.00	200	450	2000	7.4
7-5	0.99	115	450	2000	7.7
7-6	3.01	200	450	2000	4.7
7-8	1.98	100	350	2000	5.0

3.5.3 Results and Discussion

Let us initially discuss the activity of the various W-based catalysts by noting the total H_2 + CO conversions at all the experimental conditions used in run 7. Table 3.36 summarizes the conversions and the selectivity for forming C_5+ products. It should be further noted that, as explained previously in Section 2.4, the accuracy of conversion and selectivity values less than 10% is poor. However, some interesting points may be seen in Table 3.36. The addition of S increases the activity of all W-based catalysts. This enhancement in activity is quite large for Ni-W catalysts where the % H_2 + CO conversion over NWK-S and NW-S is 2 to 5 times greater than over NWK-R and NW-R respectively. At all experimental conditions the NWK-S catalyst gives the highest H_2 + CO conversion, and the NW-S catalyst gives the next highest value. In general, the activity of all the W-based catalysts for FT is low, e.g. the largest conversion observed, on the NWK-S catalyst, was only 40.7% at a reaction temperature of 449°C, a pressure of 2.1 MPa, a low space-velocity of 114 V/V/h and a H_2/CO ratio equal to 0.99; conditions which are quite severe when compared to those used with other catalysts.

The selectivity to C_5+ products is generally largest on the WK-R catalyst, and this selectivity decreases slightly for the corresponding sulfided WK-S catalyst. The addition of Ni to WO_3/Al_2O_3 decreases the selectivity, and depending on whether the Ni-W catalyst is promoted with alkali or not, two different cases arise. For the unalkalized catalyst the selectivity is greater with the reduced catalyst, i.e., NW-R > NW-S;

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[1] Accurate experimental conditions for each reactor and detailed results are given in the tables for run 7 in Appendix D, pages 182 to 200.

[2] Experiment 7-7 included results only for the MoS_2 catalyst which has been discussed in Section 3.4.

Table 3.36

Activity and Selectivity of W-Based Catalysts

Activity -- conversion = % total H_2 + CO converted
Selectivity = % CO converted to C_5^+ products

Catalyst	NWK-R	NWK-S	NW-R	NW-S	WK-R	WK-S
Experiment[1]						
7-1	3.4 (27.8)[2]	13.8 (46.5)	2.6 (33.3)	8.6 (0+)	2.6 (79.2)	9.0 (14.5)
7-2	6.1 (8.0)	19.6 (12.5)	3.7 (36.5)	16.2 (0+)	2.6 (58.2)	3.6 (14.9)
7-3	15.6 (0.01)	33.2 (13.0)	3.9 (0+)	29.5 (2.1)	2.2 (11.2)	3.8 (0+)
7-4	9.7 (2.7)	23.0 (27.1)	6.7 (26.6)	22.1 (2.5)	6.2 (71.4)	7.8 (62.8)
7-5	16.1 (1.5)	40.7 (31.6)	7.8 (0+)	27.2 (0+)	10.9 (69.0)	11.0 (37.1)
7-6	4.0 (0+)	22.5 (30.3)	4.2 (0+)	10.4 (0+)	2.5 (38.4)	3.7 (30.0)
7-8	2.9 (60.5)	12.1 (77.0)	3.2 (58.2)	5.7 (15.1)	3.1 (90.8)	3.4 (83.9)

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[1] Experimental conditions have been given in Table 3.35.

[2] ( ) = selectivity

whereas for the alkalized catalyst we have NWK-S > NWK-R. The observations regarding the activity and selectivity trends of W-based catalysts are consistent over most of the experimental conditions used by us; these results may therefore be important for formulating S resistant catalysts.

Besides the important trends discussed above, some interesting results were obtained regarding C_3 and C_4 hydrocarbons. The olefin/paraffin ratio was largest for the WK-R catalyst, e.g., for this catalyst the C_3H_6/C_3H_8 ratio was usually close to or greater than 1, whereas for all other catalysts it was always less than 1. Sulfiding a catalyst always enhanced paraffin formation. Furthermore, addition of Ni increased paraffin formation and addition of alkali usually increased olefin production. A typical example of the ratios is given in Table 3.37.

Table 3.37

C_3 and C_4 Olefin/Paraffin Ratios[1] on W-Based Catalysts

T = 450°C, P = 2.0 MPa, SV = 115 V/V/h, H_2/CO = 1.0

Catalyst	WK-R	WK-S	NW-R	NW-S	NWK-R	NWK-S
$\frac{\text{propylene}}{\text{propane}}$	0.90	0.23	0.03	0.002	0.28	0.01
$\frac{\text{butenes}}{\text{butanes}}$	0.89	0.24	0.08	0.05	0.45	0.07

The WK-R catalyst usually produced more iso-butane than n-butane and more iso-butene than 1-butene or cis-2-butene; formation of trans-2-butene was always negligibly small. Addition of sulfur, WK-S catalyst, produced approximately equal amounts of iso-butene. The sulfided and unsulfided Ni-W catalysts generally produced more n-butane than iso-butane but always formed larger amounts of iso-butene than other C_4 olefins. It seems then that the addition of S or Ni to a tungsten catalyst reduces the latter's propensity to form branched C_4 hydrocarbons.

Let us now compare the results on the sulfided Ni-W catalysts with those on the sulfided Co-Mo catalysts. Table 3.38 gives a comparison at similar experimental conditions.

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[1] C_2H_4 and C_2H_6 peaks could not be resolved during run 7. Therefore C_2 hydrocarbon values reported are a sum of $C_2H_4 + C_2H_6$.

Table 3.38

Comparison of Sulfided Ni-W and Co-Mo Catalysts

T = 350°C, P = 2 MPa, SV = 200 V/V/h, H_2/CO = 2

Catalyst	NWK-S	CMK-S	NW-S	CM-S
Weight, g	49.5	36.1	46.9	34.3
H_2 conversion, %	10.4	45.0	3.7	52.0
CO conversion, %	20.7	71.0	18.2	87.0
Total H_2 + CO conv., %	13.8	53.8	8.6	63.4
CO conv. to hydc., %	16.1	43.0	7.8	44.0
Selectivity, % CO converted to:				
CH_4	16.9	18.4	35.6	30.3
C_2	9.5	21.1	20.4	24.9
$C_3 + C_4$	5.0	7.2	4.5	2.6
C_5+	46.5	13.8	0	0
CO_2	22.1	39.5	39.5	42.2

The Co-Mo catalysts are more active than the Ni-W catalysts. However, there is a remarkable similarity in product selectivity for the unalkalized Ni-W and Co-Mo catalysts. Furthermore, the addition of alkali to these catalysts produces a similar selectivity trend. The main effect of the alkali promoter is to decrease the formation of light hydrocarbons, CH_4 and C_2, and increase the selectivity to C_3+, and especially C_5+, hydrocarbons. Thus for the Ni-W catalyst, like in the case of Co-Mo, there seems to be an alkali-sulfur interaction which promotes the formation of condensed products. It should also be noted that the selectivity for CO_2 production is large in all cases.

The problem of the W-based catalysts used by us is one of low activity. As stated previously, the highest conversion observed during this set of experiments was 41% on the NWK-S catalyst at 449°C, a pressure of 2.1 MPa, a space-velocity of 114 V/V/h and a H_2/CO ratio of 0.99. In comparison, the same conversion of 41% was observed on the CMK-S catalyst at much less severe conditions: 302°C, 1.5 MPa pressure, a space-velocity of 198 V/V/h and a H_2/CO ratio of 2.1. The Co-Mo-based catalysts gave considerably higher conversions under different conditions. It was also noted that on sulfiding the Ni-W catalysts the activity was considerably greater than that of the reduced, unsulfided catalysts. Such a large dependence of activity on catalyst sulfidation was not obtained with the Co-Mo catalysts. In fact, for several experimental conditions, sulfided and unsulfided Co-Mo catalysts showed similar catalytic activity.

A recent XPS study (75) on alumina supported tungsten and nickel-tungsten catalysts indicated several differences in surface changes after pre-treatment compared to changes after similar pre-treatments on Co-Mo/ Al_2O_3 catalysts. When the W-based catalysts were reduced at 450 to 500°C in H_2, W remained in the +6 oxidation state with no reduction even after prolonged treatment. Nickel, if present, was readily reduced to the metal. The reduction of Ni leveled off at 75% indicating that 25% of the surface Ni was probably present as irreducible Ni^{2+} that interacted with Al_2O_3 to form a "surface spinel" (76). Similar reduction studies (64) on alumina supported Mo-based catalysts showed that Mo (VI) was reduced to Mo (V) and Mo (IV) but Co remained unreduced.

A similar difference may be noted for the sulfided catalysts. Ng and Hercules (75) showed that the alumina supported W and Ni-W catalysts could be completely sulfided in a 9% H_2S/H_2 mixture at 350°C with the formation of WS_2, NiS, and Ni_3S_2 compounds. The Co-Mo/Al_2O_3 catalysts, on the other hand, could only be partially sulfided (64,67), and though some MoS_2 may be formed (64) it is probable that oxy-sulfides of Mo also occur (67). Furthermore, unlike the case of Ni in the W catalyst, evidence of discreet cobalt sulfides is not available (64, 67) though it has been suggested that Co is present as Co_9S_8 (69).

The low activity of the "reduced" unsulfided W-based catalysts may be due to the fact that W (VI) remains unreduced. Moreover, the fact that some Ni may be present in the metallic form does not seem to benefit catalytic activity. On sulfiding, the oxidation state of W changes from +6 to +4, and all sulfided W-based catalysts are seen to be more active. If one again assumes that, like in the case of Co-Mo catalysts, adjacent surface anionic vacancies are necessary for FT activity then one can infer that more such vacancies are available for the sulfided catalysts when W (IV) is present than for the "reduced" catalyst when W (VI) is present. The presence of Ni and alkali is seen to further enhance the activity of the sulfided catalyst; this promotion may take place either by increasing the number of vacancies or by influencing the vacancies so that they become more active for CO hydrogenation. But before catalyst promotion can occur, it seems that the presence of W (IV) is required. Therefore the activity of sulfidic and oxidic W-based catalysts is different.

In the case of Co-Mo/Al_2O_3, hydrogen reduction reduces Mo (IV) to Mo (V) and Mo (IV), probably giving rise to surface anion vacancies, and this may be the reason why reduced Co-Mo/Al_2O_3 catalysts are active for FT synthesis. As sulfiding of Co-Mo/Al_2O_3 catalysts is partial and as sulfided catalysts also contain reduced Mo species, the number of vacancies may not be drastically changed after sulfiding and hence the activity of oxidic and sulfidic Co-Mo/ Al_2O_3 is close. The sulfidation and the presence of alkali, however, probably influences the active site so that the catalytic selectivity is changed.

The similarity in the selectivities of the sulfided Co-Mo and Ni-W catalysts, as shown in Table 3.38, is intriguing. Their large difference in activities may be postulated as being due to the difference in the number of surface anionic vacancies; but the similarity in selectivity may be due to similar influences being exerted on the site by the environment. This speculation is attractive since, besides metallic catalysts such as Co, Ru, and Fe, non-metallic catalysts which offer surface anionic vacancies in a particular environment may be tailored to produce sulfur resistant FT catalysts.

3.5.4 Summary

- The activity of W-based catalysts for the FT synthesis was low. The sulfided catalysts were more active than the corresponding reduced, unsulfided catalysts. The most active catalyst was sulfided, alkali-promoted Ni-W/Al_2O_3.

- The highest selectivity to C_5+ products was obtained with the reduced, unsulfided WK-R catalyst which showed the poorest activity.

- Of the Ni promoted catalysts, NWK-S gave the best selectivity for condensed products.

- Though their activity was low, the sulfided Ni-W catalysts showed a similar selectivity pattern as the sulfided Co-Mo catalysts.

3.6 Alumina Supported Ruthenium Catalysts

3.6.1 Catalyst Pre-Treatment and Sulfiding

The catalyst used was 1% Ru supported on 60 to 140 mesh γ-Al_2O_3 and was supplied in the reduced state by Engelhard. The preparation technique and reduction procedure used by Engelhard were identical to those used by them to make commercial Ru/Al_2O_3 catalysts. The catalyst was used (a) without any promoter, and (b) after being impregnated with KOH so that the alkali content, calculated as K_2O, was 10% by weight of the total catalyst.

The reactors, after being loaded with the catalysts as shown in Table 3.39, were assembled on the unit and flushed and pressure tested with He. The catalysts in all the reactors were initially treated in flowing H_2, 700 V/V/h, at atmospheric pressure and 350°C for 4 h. The temperature was then reduced to 210°C, and the catalysts were kept overnight at 210°C in H_2 flowing at 350 V/V/h. Finally, the catalysts were treated at atmospheric pressure and 200°C in a 2:1 gas mixture of H_2/CO, 300 V/V/h, for 24 h. At the end of the pretreatment, all the reactors were flushed with He, and reactor 5, 6, and 7 were shut off and kept under He at 500 kPa.

Catalysts in reactors 1 and 3 were sulfided for 3.5 h at atmospheric pressure and 200°C with a 2:1 mixture of H_2/CO containing 260 ppm sulfur and flowing at a space velocity of 300 V/V/h. Reactors 2 and 4 were sulfided under identical conditions for 20.5 h. Hydrogen sulfide was detected coming out of reactors 1 and 2 during sulfiding.

Table 3.39 summarizes the catalysts and the pre-treatment procedure.

Table 3.39

Summary of Catalysts in Run 8

Symbol	Reactor	Catalyst[1]	Pretreatment
Ru-R	7	1% Ru/Al_2O_3	Reduced in H_2
Ru-S1	1	1% Ru/Al_2O_3	Reduced in H_2 and then sulfided for 3.5 h
Ru-S2	2	1% Ru/Al_2O_3	Reduced in H_2 and then sulfided for 20.5 h
RuK-R	5 and 6	1% $Ru/Al_2O_3 + K_2O$	Reduced in H_2
RuK-S1	3	1% $Ru/Al_2O_3 + K_2O$	Reduced in H_2 and then sulfided for 3.5 h
RuK-S2	4	1% $Ru/Al_2O_3 + K_2O$	Reduced in H_2 and then sulfided for 20.5 h

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[1] 50 cm^3 of 60-140 mesh particles were used in each reactor. The weight of catalyst 1% Ru/Al_2O_3 loaded into each reactor was 26.8 g (dry basis), whereas the weight of catalyst 1% $Ru/Al_2O_3 + K_2O$ in each reactor was 30.0 g (dry basis).

At the end of the run, a longitudinal sulfur gradient analysis was attempted, as in the case of catalysts studied previously, using the Dietert technique. This technique, however, could not be used because the chlorine (0.06 wt %) on the support interfered with the sulfur analysis. A more complex in-house combustion-gravimetric technique, using a Parr bomb, was necessary, and therefore only selected catalyst sections were analyzed (Table 3.40) to indicate the sulfur levels in the various reactors. In Table 3.40, section 1 corresponds to the first 5 cm of the inlet side of the reactor, section 2 corresponds to the next 5 cm of reactor length, etc.

Table 3.40

Longitudinal Sulfur Distribution in Catalyst Beds for Run 8

Catalyst	Ru-S1	Ru-S2	RuK-S1	RuK-S2
Section	Reactor 1 % S by wt	Reactor 2 % S by wt	Reactor 3 % S by wt	Reactor 4 % S by wt
1	0.19	0.35	0.72	0.55
2	—	—	0.33	—
3	—	—	—	—
4	0.16	—	0.29	—
5	—	—	—	—
6	0.16	0.18	0.37	0.21
7	—	—	—	—
8	—	—	0.18	0.27
9	—	—	—	—
10	0.21	0.40	0.18	0.53
11	—	0.15	0.18	—
12	—	—	—	—
13	—	—	—	—
14	—	—	—	—
15	0.17	—	0.23	0.18
16	—	—	—	—
17	0.23	0.17	0.07	0.29
18	0.18	0.19	0.07	0.20
19	—	0.25	0.02	0.37

Catalysts Ru-S1 and RuK-S1 were treated identically, but the sulfur levels near the exit were small in the case of RuK-S1, whereas the sulfur levels were more uniform in the case of Ru-S1. This may be important because the presence of alkali seems to affect the sulfur gradient by keeping more of the sulfur near the entrance and the initial part of the reactor. After sulfur was added for a longer time period, this particular effect of alkali was not found, and catalyst Ru-S2 and RuK-S2 both contained quite uniform sulfur levels throughout the reactor. It must be noted that during sulfiding, H_2S was detected to be coming out of reactors 1 and 2. Furthermore, gases coming out of reactors 1 and 4 were analyzed after Experiments 8-1 and 8-2. Sulfur was detected in the exit gases, and it was found to be mainly CH_3SH (5 to 35 ppm) with some CS_2 and only trace quantities of H_2S. The sulfur on the catalyst seems to react with

CO and H_2. It may be inferred that there was some movement of sulfur on the catalysts during the experiments, and hence the sulfur gradient obtained after the run was completed may have been quite different from the gradient just after the sulfiding procedure. In any case, the catalysts, especially in reactors 2 and 4, contained sufficient sulfur to warrant the assumption that almost all the surface Ru had been exposed to sulfur.

3.6.2 Experiments Performed and Comments on the Reproducibility of Results

Before discussing the complete run, let us list the experiments in the order that they were performed. The following table gives the experimental conditions and duration of each test:

Table 3.41

Experimental Conditions[1] for Run 8

Experiment	H_2/CO	SV, V/V/h	T, °C	P, kPa	Time, h
8-1	2.06	210	240	2200	5.4
8-2	2.01	200	225	2200	6.1
8-3	2.94	200	240	2200	4.6
8-4	2.00	200	240	2200	5.0
8-5	2.04	200	240	3100	4.8
8-6[2]	0.97	197	243	2200	2.9
8-7	2.02	200	300	3100	5.2
8-8	2.05	200	350	3100	4.0
8-9	2.06	200	240	2200	4.5
8-10	2.01	200	240	2200	4.3

Before starting Experiment 8-1, the catalysts were flushed with He. Between Experiments 8-1 and 8-2, the catalysts were again exposed to flowing He overnight at the conditions of Experiment 8-1. However, it was decided at the end of Experiment 8-2 to expose the catalysts, after each experiment, to flowing H_2 at 200°C (except after Experiment 8-9) and the pressure of the preceeding experiment until the next experiment was started on the following day. The explanation of the treatment after experiment 8-9 is given later. Hydrogen treatment was used to try and keep the metal surface as free from carbon deposits as possible, and hence enable comparisons between experiments to be made. For example, Experiments 8-1 and 8-4 were carried out under similar conditions, and as shown in Table 3.42 the results from reactor 7, containing catalyst Ru-R, are close. Alkalized and sulfided catalysts are not directly compared for different experiments as the chances for surface changes due to sulfur or alkali movement are possible. However, the

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[1] Accurate experimental conditions for each reactor and detailed results are shown in the tables for Run 8 in Appendix D, pages 201 to 221.

[2] Experiment performed only with catalyst Ru-R in reactor 7.

Table 3.42

Comparison of Results from Reactor 7

Catalyst: 1% Ru/Al_2O_3

Experiment	8-1	8-4
Pressure, kPa	2200.00	2200.00
Space-velocity, V/V/h	212.20	194.70
Inlet H_2 flow, cm^3/min	119.04	108.40
Inlet CO Flow, cm^3/min	57.79	54.20
Reaction temperature, °C	245.00	245.00
H_2/CO	2.06	2.00
Avg. contraction, %	84.73	87.70
CO_2-free contraction, %	85.52	88.69
H_2 converted, cm^3/min	103.25	99.42
H_2 converted, µmoles/min	4218.87	4055.47
H_2 conversion, %	86.73	91.71
CO converted, cm^3/min	51.87	47.35
CO converted, µmoles/min	2119.39	1931.49
CO conversion, %	89.75	87.35
Total H_2 + CO conversion, %	87.72	90.26
H_2 usage ratio	0.67	0.68
Gaseous products, µmoles/min		
CH_4	85.84	78.45
$C_2H_6 + C_2H_4$	9.16	6.16
C_3H_8	7.44	5.06
C_3H_6	18.63	7.42
$i-C_4H_{10}$	0.03	0.03
$n-C_4H_{10}$	5.98	3.80
$1-C_4H_8$	10.64	7.32
$i-C_4H_8$	0.04	0.02
$cis-2-C_4H_8$	1.33	0.49
CO_2	57.62	65.91
Selectivity, % CO converted to:		
C_5+	85.26	87.52
CH_4	4.05	4.06
CO_2	2.71	3.41

reproducibility within any particular experiment was shown to be good due to the close match of results obtained in reactors 5 and 6, each containing the RuK-R catalyst.

The only experiment in which results from reactors 5 and 6 differed considerably was Experiment 8-7. It was felt that this difference could have been due to changes taking place, after a 3100 kPa pressure experiment (Experiment 8-5), on the catalyst surface regarding the position of the large amount of alkali; and that these changes were not identical in the two reactors at that time. However, after Experiment 8-7 and the overnight treatment in H_2, the catalysts in the two reactors 5 and 6 behaved very similarly in Experiment 8-8. The possible changes that may have occurred on the surface may be important especially since the catalysts seemed to have come to a state which gave similar results. These observations will be discussed later.

Finally, problems were encountered after Experiment 8-8 which was conducted at a high temperature (350°C) and a high pressure (3100 kPa). As shown in Table 3.43 for the Ru-R catalyst, conversions in Experiment 8-9 were low and the selectivities were quite different from those obtained in Experiment 8-1 which was performed at similar conditions. It was felt that carbonaceous residues could have formed during the high temperature experiment, and that their presence probably caused the changes in catalytic behavior. After Experiment 8-9, the catalyst was exposed to flowing H_2 at 350°C. The results of Experiment 8-10 indicate that this overnight treatment in H_2 was helpful in restoring a significant amount of activity, and the selectivity was close to that observed in Experiment 8-1. Further treatments in H_2 were not done, but they probably would have restored the initial activity of the catalyst. Similar restorative effects of H_2 were found by Karn et al. (77) on 0.5% Ru/Al_2O_3 used in FT synthesis. Sulfided and alkalized catalysts, however, showed low activities in Experiments 8-1, 8-9, and 8-10, all of which were carried out at 2200 kPa. And a regenerative H_2 effect was not observed in their cases.

3.6.3 Results and Discussion

In most of the following discussion, when comparing the results of sulfided and unsulfided catalysts, catalysts Ru-S2 and RuK-S2, which were sulfided for the longest time, 20.5 h, will be used for comparison. Though the behavior of catalysts sulfided for 3.5 h or 20.5 h was generally similar to each other, using the catalyst sulfided for a longer time for comparative purposes seems to be a more conservative approach.

Though the addition of alkali or sulfur to a 1% Ru/Al_2O_3 catalyst generally reduced the activity of the catalyst, certain important points may be deduced from our results. Table 3.44 shows some significant changes of catalytic behavior as a result of increasing pressure.

Increasing the pressure from 2.2 MPa to 3.1 MPa brings about a six to seven fold increase in the activity of sulfided and alkalized catalysts. At the low pressure, the Ru-R catalyst is about 9 times more active than the corresponding sulfided catalyst Ru-S2. On increasing the pressure

Table 3.43

Comparison of Active, Deactivated and H_2 Treated 1% Ru/Al_2O_3 Catalyst - Reactor 7

$H_2/CO \simeq 2.0$

Experiment	8-1	8-9	8-10
	Active Catalyst In First Experiment	Deactivated[1] After Experiment 8-8 at 350°C	After Overnight H_2 Treatment at 350°C
Pressure, kPa	2200.00	2200.00	2200.00
Space-velocity, V/V/h	212.20	200.30	197.20
Inlet H_2 flow, cm^3/min.	119.04	112.37	109.73
Inlet CO flow, cm^3/min	57.79	54.55	54.59
Reaction temperature, °C	245.00	241.00	242.00
Avg. contraction, %	84.73	28.11	64.70
CO_2-free contraction, %	85.52	28.34	65.27
H_2 converted, cm^3/min	103.25	32.63	72.65
H_2 converted, µmoles/min	4218.87	1320.00	2948.88
H_2 conversion, %	86.73	29.03	66.21
CO converted, cm^3/min	51.87	17.27	36.76
CO converted, µmoles/min	2119.39	698.85	1491.75
CO conversion, %	89.75	31.66	67.32
Total H_2 + CO conversion, %	87.72	29.89	66.57
H_2 usage ratio	0.67	0.65	0.66
Gaseous Products, µmoles/min			
CH_4	85.84	44.96	49.72
$C_2H_6 + C_2H_4$	9.16	3.37	3.27
C_3H_8	7.44	3.41	3.11
C_3H_6	18.63	9.14	11.02
$i-C_4H_{10}$	0.03	0.03	0.02
$n-C_4H_{10}$	5.98	3.56	3.69
$1-C_4H_8$	10.64	7.35	9.80
$i-C_4H_8$	0.04	0.02	0.04
$cis-2-C_4H_8$	1.33	0.22	0.29
CO_2	57.62	15.96	38.03
Selectivity, % CO converted to:			
C_5+	85.26	78.50	87.11
CH_4	4.05	6.43	3.33
CO_2	2.71	2.28	2.55
CO conv. to C_5+/CO conv. to hydc. gas	7.09	4.08	8.43

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[1] Note: H_2 treatment at 200°C after Experiment 8-8 was insufficient to reactivate the catalyst.

Table 3.44

The Effect of Pressure on Activity and Selectivity Ru/Al_2O_3 Catalysts

T = 240°C, SV = 200 V/V/h, H_2/CO = 2.0

	P = 2.2 MPa				P = 3.1 MPa			
Catalyst	Ru-R	Ru-S2	RuK-R	RuK-S2	Ru-R	Ru-S2	RuK-R	RuK-S2
H_2 + CO conv., %	87.7	9.4	7.4	4.8	95.5	52.9	49.1	35.8
Conv. Ratio = unsulfided catalyst / sulfided catalyst	9.3		1.5		1.8		1.4	
Selectivity, % CO converted to:								
C_5+	85.26	99.66	97.22	97.31	99.63	99.9	97.24	99.81
CH_4	4.05	0.09	1.56	0.84	0.15	0.02	0.08	0.05
CO_2	2.71	0	0.44	0.87	0	0.06	2.51	0.09

to 3.1 MPa, this activity difference is reduced from a factor of 9 to 1.8. As the activity of sulfur-poisoned Ru/Al_2O_3 catalyst is significantly improved by increasing the reactant pressure, it may be possible to offset catalyst deactivation due to the presence of sulfur by working at pressures above 3 MPa. An advantage of Ru catalysts is that, unlike Co and Fe catalysts, they can be used at high pressures of synthesis gas.

The activity of the alkalized catalyst RuK-R is 12 times less than that of Ru-R at 2.2 MPa. But the addition of sulfur to RuK-R reduces the activity only by a factor of 1.5, unlike the drastic deactivation observed in the case of the unalkalized catalyst. Hence, there is no significant deactivation by sulfur for the alkalized catalyst. Increasing the pressure to 3.1 MPa increases the activity of both RuK-R and RuK-S2, so that the latter is still only 1.4 times less active than the former. Also, at the higher pressure the alkalized catalyst is only 1.9 times less active than Ru-R. As stated before, the alkalized catalyst was made by impregnating KOH, corresponding to 10% by wt K_2O, on the reduced 1% Ru/Al_2O_3. The alkali probably covered many active Ru sites leading to the poor activity of the RuK-R catalyst. It is possible that other techniques of combining Ru-K-Al_2O_3 may give a catalyst with higher activity, and one which also shows a similar resistance to deactivation by sulfur as our present RuK-R catalyst.

One explanation of the remarkable enhancement in the activity of Ru catalyst at high pressure requires the assumption that the seat of activity consists of two or more adjacent sites. If even one site is blocked the reaction cannot occur as seen by the low conversions obtained on sulfided or alkalized Ru catalysts. On increasing the reactant pressure, it may be possible to displace the site-blocking poison with a reactant, and the surface intermediate necessary for the hydrocarbon growth process may then be formed. Thus, the activity of the poisoned catalyst may be considerably higher under conditions such as high pressure when sites that have been blocked are freed. The small difference in activity between the RuK-R and the RuK-S2 catalysts is probably due to the fact that most of the sulfur interacts with the alkali which is already blocking a reaction site.

Besides a pressure effect, a significant temperature effect was observed at a pressure of 3.1 MPa for the alkalized catalyst as shown in Table 3.45.

As the temperature is increased from 240 to 300°C, the conversion over the alkalized catalyst increases from 41 to 98%. It is interesting to compare this high activity of the RuK-R catalyst with a conversion value of 6% for the same catalyst at 240°C and 2.2 MPa as stated before. It is possible that the catalyst surface is quite different at the higher pressure and temperature with more sites available for chemisorption of the reactants due to possible removal of some of the site-blocking alkali. It is also possible that chemisorption is considerably enhanced on the Ru-K surface at the high pressure and temperature conditions leading to higher conversions. The selectivity to C_5+ hydrocarbons decreases with increasing temperature with a corresponding increase in CH_4 and CO_2 formation. At the 99+% conversion levels the CO_2 formation could be due to the Boudouard reaction, causing coke to be deposited on the

Table 3.45

Comparison of Alkalized and Unalkalized Ru/Al_2O_3 Catalyst

P = 3.1 MPa, SV = 200 V/V/h, $H_2/CO = 2.0$

Temperature, °C	240		300		350	
Catalyst	Ru-R	RuK-R	Ru-R	RuK-R	Ru-R	RuK-R
H_2 + CO conv., %	95.5	41.1	99.6	97.5	99.4	98.9
Selectivity, % CO converted to:						
C_5+	99.63	95.16	82.86	68.47	16.55	30.91
CH_4	0.15	0.09	7.89	13.62	61.96	42.03
CO_2	0	4.46	5.98	8.58	21.03	15.57
Gaseous olefins:						
propylene/propane	0.01	2.33	<0.01	0.02	0.03	<0.01
butenes/n-butane	0.12	1.85	0.01	0.06	0.04	0.02

catalyst. At the highest temperature studied (350°C), the selectivity to C_5+ products is twice as high for the alkalized catalyst than the unalkalized catalyst. The gaseous products are predominantly paraffinic except in the case of the RuK-R catalyst at the lowest temperature, 240°C, studied. Condensed products from both catalysts were analyzed, and the analysis is shown in Table 3.46.

The molecular weight of the products obtained with the alkalized catalyst is greater than that obtained with the unalkalized catalyst. The unalkalized catalyst gives predominantly n-paraffins, and the percentage of n-paraffins for each carbon number is approximately the same. On the other hand, the alkalized catalyst gives liquid products which are not chiefly n-paraffins for carbon numbers less than C_{12}, and the amount of n-paraffins in the liquid product increases with carbon number for the RuK-R catalyst. It is interesting to note that this result on condensed products is quite different from the results of gaseous products with the same RuK-R catalyst, which show that significantly larger amounts of propane and n-butanes are formed rather than the corresponding olefins or branched compounds (Table 3.45).

The best results, in terms of activity and selectivity, were obtained for the Ru-R catalyst at 240°C and 3.1 MPa (Experiment 8.5). As shown in Table 3.45, a 95.5% conversion was obtained with 99.6% of the CO converted being used to form C_5+ products. Moreover, as shown in Figure 3.18, 99 wt % of the product is between C_5 and C_{25} with a maximum of 12.5 wt % at C_{10}. The normal paraffinic content of the condensed product is 90+ wt %. Thus, alumina supported Ru catalysts under appropriate experimental conditions can give high conversion to liquid paraffins with negligible gaseous products or wax (C_{25}+).

Table 3.46

Components in Condensed Product
Alkalized and Unalkalized Ru/Al_2O_3 Catalysts

T = 350, P = 3.1 MPa, SV = 190 V/V/h, H_2/CO = 2.0

Catalyst	Ru-R			RuK-R		
Carbon Number[1]	Total wt %	% n-paraffins	% Other[2]	Total wt %	% n-paraffins	% Other[2]
C_6	0.32	87.5	12.5	--	--	--
C_7	1.38	92.0	8.0	0.16	0	100
C_8	4.34	88.0	12.0	1.34	0	100
C_9	8.40	87.7	12.3	4.18	0.5	95.5
C_{10}	11.45	87.5	12.5	3.79	3.7	96.3
C_{11}	12.58	86.7	13.3	4.31	23.2	76.8
C_{12}	12.19	86.6	13.4	6.63	52.5	47.5
C_{13}	10.96	86.3	13.7	9.95	64.9	35.1
C_{14}	9.51	86.4	13.6	11.22	68.3	31.7
C_{15}	7.96	88.1	11.9	11.03	71.7	28.3
C_{16}	6.40	87.0	13.0	8.59	76.9	23.1
C_{17}	4.78	85.9	14.1	7.85	74.0	26.0
C_{18}	3.37	84.6	15.4	6.08	77.3	22.7
C_{19}	2.24	83.5	16.5	4.93	76.7	23.3
C_{20}	1.43	83.2	16.8	3.89	79.2	20.8
C_{21}	0.72	84.7	15.3	2.73	84.2	15.9
C_{22}	0.43	89.6	10.4	1.37	97.8	2.2

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[1] Break-down of various components after C_{22} have not been given because as the molecular weight of the components increases the chromatograph resolution becomes inaccurate.

[2] Probably olefins and branched paraffins.

Figure 3.18

Distribution of Condensed Products
1% Ru/Al_2O_3 Catalyst

T = 241°C, P = 3100 kPa, SV = 193 V/V/h, H_2/CO = 2.0

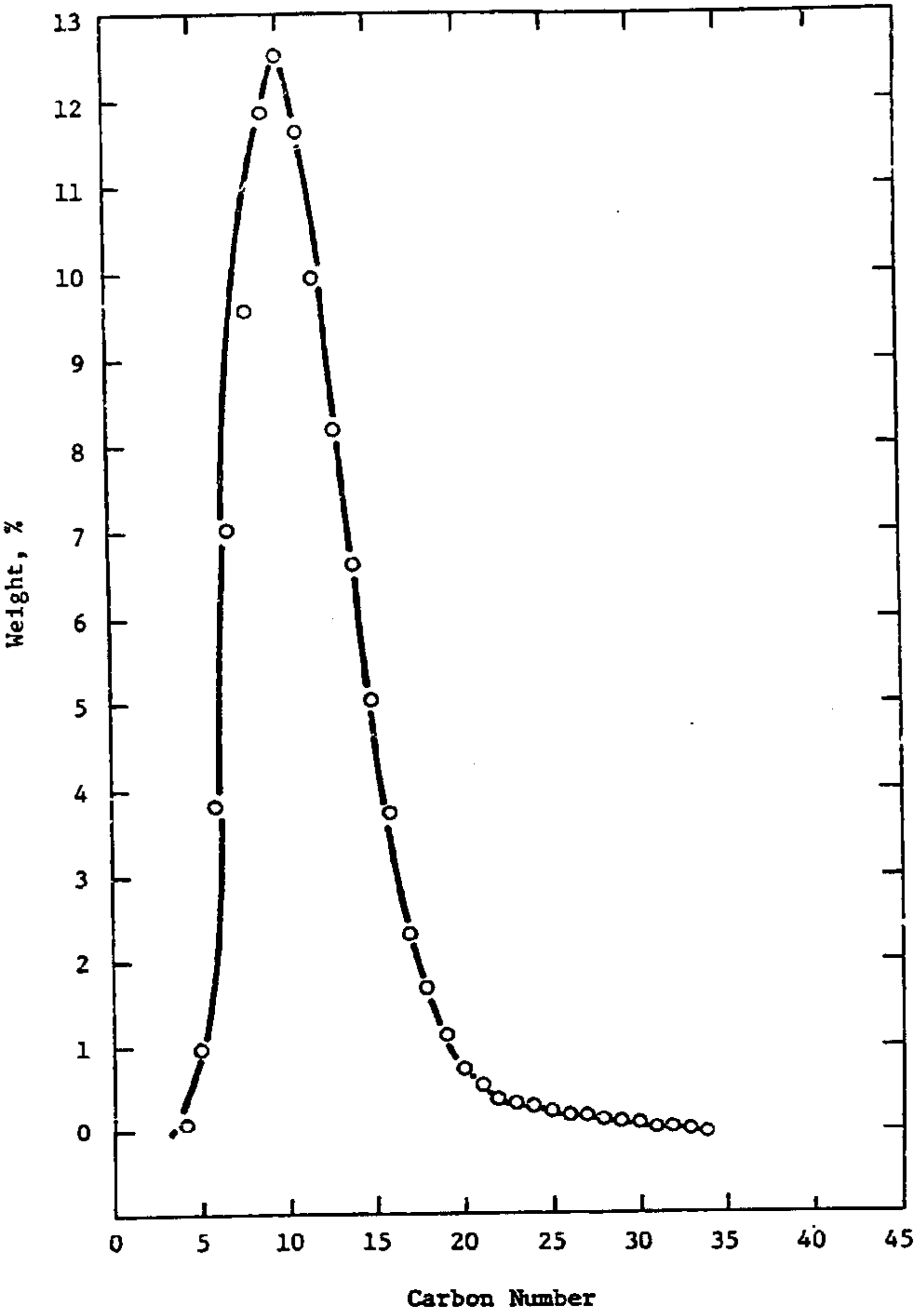

Table 3.47 shows the effect of H_2/CO ratios on the performance of the unsulfided, unalkalized 1% Ru/Al_2O_3 catalyst.

Table 3.47

The Effect of H_2/CO Ratio
1% Ru/Al_2O_3

T = 244°C, P = 2.2 MPa, SV = 200 V/V/h, Catalyst = Ru-R

H_2/CO ratio	0.97	2.06	2.94
H_2 + CO conv.,%	44.6	87.7	90.5
Selectivity, % CO converted to:			
C_5+	90.02	85.26	35.11
C_3 + C_4	5.35	7.12	6.07
C_2	0.40	0.86	21.06
CH_4	1.75	4.05	37.71
CO_2	2.48	2.71	0.05
Gaseous olefins:			
propylene/propane	3.98	2.50	0.002
butenes/n-butane	3.05	2.00	0.002
iso-butane/n-butane	0.01	0.005	1.03
Normal paraffins in C_5-C_{22} hydrocarbons, wt%	79	81	90

The effect of H_2/CO ratios on both activity and selectivity is quite large. A H_2/CO ratio of 1 gives low conversions but gives a high selectivity to liquid products; on increasing the ratio to 2 the conversion increases substantially.but the selectivity remains close to that obtained with $H_2/O = 1$. Finally, when the H_2/CO ratio is increased to 3 high conversions are obtained, but the selectivity to condensed products is reduced with large quantities of CH_4 and C_2 hydrocarbons being formed. Also at $H_2/CO = 3$ only small amounts of gaseous olefins are detected,but as much iso-C_4H_{10} as n-C_4H_{10} is formed. The effect of H_2/CO ratios on the condensed product distributions is shown in Figure 3.19. Most of the products are between C_5 to C_{25} with little wax formation. The molecular weight of the product increases as the H_2/CO ratio decreases. From the above results, it can be seen that in order to get high conversions to C_5 to C_{25} hydrocarbons, a H_2/CO ratio of 2 should be used with the 1% Ru/Al_2O_3 catalyst.

Finally, let us compare the selectivity of the sulfided catalyst, Ru-S2, with catalyst Ru-R under experimental conditions in which the latter catalyst gives large quantities of gaseous hydrocarbons. Two such conditions were investigated by us; a high temperature conditions (Experiment 8-9) and a condition with a high H_2/CO ratio of 2.9 (Experiment 8-3). The comparisons are given in Table 3.48.

Figure 3.19

Distribution of Condensed Products
1% Ru/Al_2O_3 Catalyst

T = 244°C, P = 2200 kPa, SV = 200 V/V/h

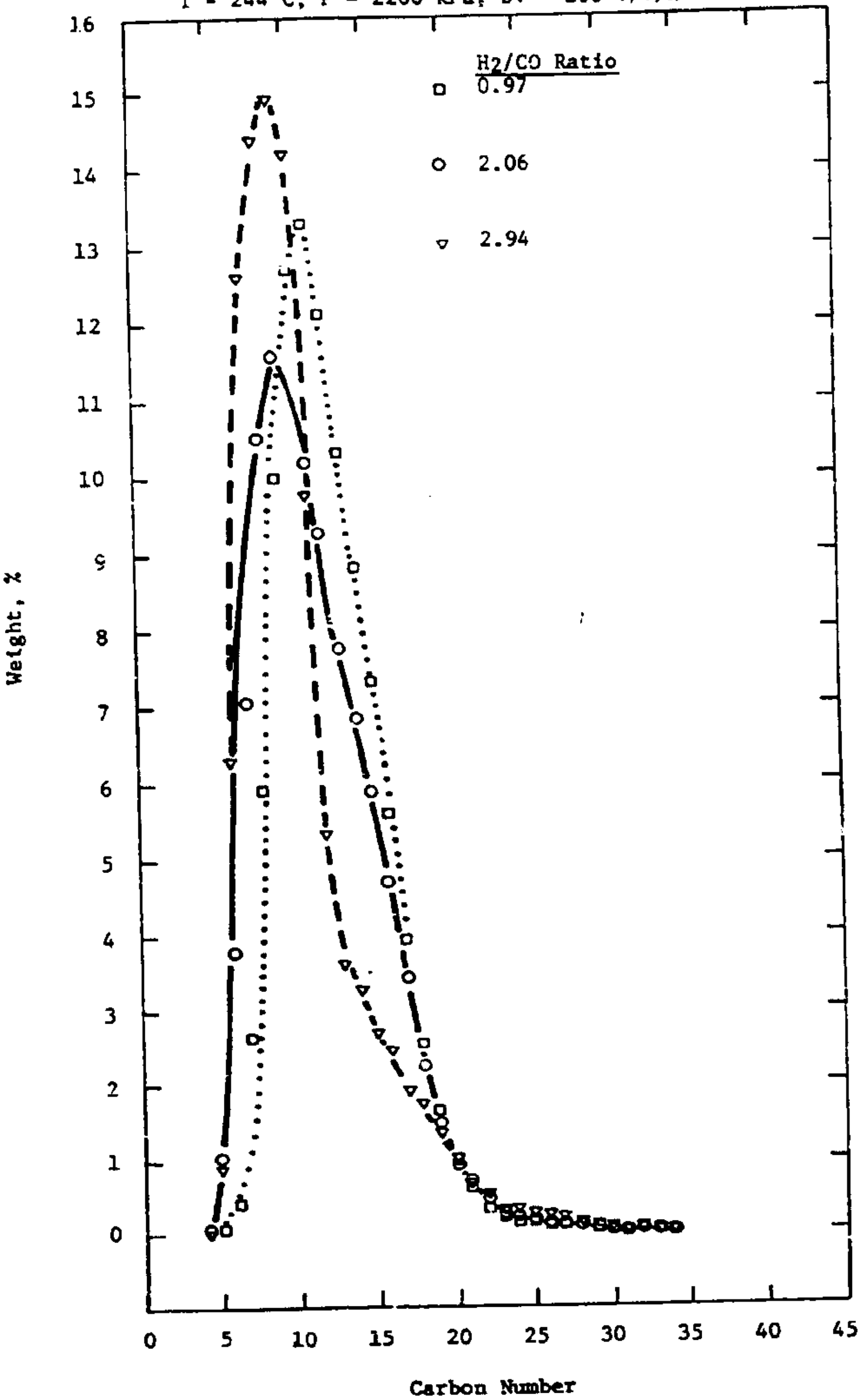

Table 3.48

Comparison of Sulfided and Unsulfided Ru/Al_2O_3 Catalysts

Case A: T = 350°C, P = 3.1 MPa, SV = 200 V/V/h, H_2/CO = 2.05

Case B: T = 240°C, P = 2.2 MPa, SV = 200 V/V/h, H_2/CO = 2.94

	Case A (High Temp)		Case B (High H_2/CO Ratio)	
Catalyst	Ru-R	Ru-S2	Ru-R	Ru-S2
H_2 + CO conv., %	99.4	25.25	90.5	1.75
Selectivity, % CO converted to:				
C_5+	16.55	80.84	35.11	98.65
CH_4	61.96	7.86	37.71	0.21
CO_2	21.03	14.34	0.05	1.00

Under both experimental conditions, high temperature and high H_2/CO ratio, 1% Ru/Al_2O_3 gives a poor selectivity to C_5+ products. The sulfided catalyst, however, though low in activity does not show any drastic reduction in its condensed product selectivity. The addition of sulfur seems to prevent the formation of CH_4. Furthermore, under most experimental conditions, the gaseous olefin/paraffin ratio is larger for the Ru-S2 catalyst than the Ru-R catalyst. And, at several conditions, more iso-butene is formed than any other C_4 hydrocarbon with the Ru-S2 catalyst. This is not the case with the Ru-R catalyst.

Let us now compare the catalytic behavior of the 1% Ru/Al_2C_3 catalyst with that of the precipitated iron-based and cobalt-based catalysts which have been discussed in Sections 3.1.3 and 3.2.3. Table 3.49 gives a sample comparison.

The Co-based catalyst was the most active catalyst, but it formed large quantities of C_{26}+ hydrocarbons at 1.6 MPa pressure. The Fe-based catalyst not only formed much wax but also produced a large amount of CO_2 via the water-gas shift reaction. On the Ru catalyst most of the CO was converted to liquid hydrocarbons with little wax or gas formation. Therefore, 1% Ru/Al_2O_3 was the most efficient catalyst for converting CO to hydrocarbons useful for liquid fuels. The condensed product, in all cases, was mostly n-paraffinic in nature. The Co-based catalyst gave the least amount of olefinic product.

X-ray diffraction measurements were carried out on the reduced, unused 1% Ru/Al_2O_3 catalyst. No Ru peaks were observed indicating that the Ru particle size was probably less than 3 nm. X-ray diffraction measurements

Table 3.49

Comparison of Supported Ru Catalyst with Precipitated Iron-based and Cobalt-based Catalysts

Catalyst	1% Ru/Al_2O_3	Fe-based	Co-based
Weight, g	26.8	39.4	29.8
Volume, cm^3	50.0	40.0	50.0
Reaction temperature, °C	245.0	239.0	194.0
Reaction pressure, MPa	2.2	2.3	1.6
H_2/CO ratio	2.0	1.5	2.0
Space-velocity, V/V/h	212.0	257.0	216.0
CO_2-free contraction, %	85.5	71.0	83.8
H_2 conversion, %	86.7	55.5	86.3
CO conversion, %	89.6	98.5	85.3
CO converted to hydc., %	87.3	58.5	80.2
Selectivity, % CO converted to:			
CH_4	4.1	3.3	8.7
C_2	0.4	4.4	2.2
$C_3 + C_4$	7.5	8.8	8.1
C_5+	85.3	42.8	75.0
CO_2	2.7	40.7	6.0
CO conv. to C_5+/CO conv. to gas[1]	5.8	0.7	3.8
Wt % in condensed products:[2]			
C_5 to C_{11}	55.3	14.2	17.0
C_{12} to C_{25}	44.4	60.2	53.0
C_{25}+	0.3	25.6	30.0
Total n-paraffins in condensed products, %	82	82	95+
Gaseous olefins:			
C_2H_4/C_2H_6	—[3]	0.1	~ 0
C_3H_6/C_3H_8	2.5	2.3	0.8
C_4H_8/n-C_4H_{10}	2.0	1.9	0.4

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[1] CH_4 to C_4 hydrocarbons + CO_2.

[2] See Figures 3.5, 3.12, and 3.19.

[3] C_2H_4 and C_2H_6 peaks were not resolved during run 8.

were then also carried out at the end of the run on certain sections of the used Ru-R catalyst (reactor 7). The catalyst in reactor sections 1, 4, 8, and 14 (see Table 3.40) were studied. Catalysts in sections 1 and 4 gave broad γ-Al_2O_3 peaks, but Ru peaks were not observed. The results from section 8 showed that the γ-Al_2O_3 had changed to a more crystalline α monohydrate form, and again no Ru peaks were observed. The diffraction pattern of the sample from section 14 again gave peaks of α-Al_2O_3, but now peaks corresponding to Ru were also present. The metal particle size was estimated from the x-ray result for section 14 to be 10 nm. These observations indicate a dramatic change in the Al_2O_3 form and possibly a growth of Ru particle as one goes from reactor entrance to exit. The thermocouple placed half-way into the catalyst had shown values close to the reactor furnace temperature. Moreover, previous work by us had indicated (Section 2.5) that severe temperature gradients are not present in our system. However, the conditions for Experiment 8-8, 350°C and 3.2 MPa pressure, may have been severe enough to cause temperature gradients, hot spots, and metal particle sintering. Sintering of Ru particles and the change in the form of alumina could also be partly due to the presence of water. It is interesting to note that there were no significant changes near the top, i.e. where the amount of product water was probably not large enough.

Though Ru catalysts have been used in the past to study wax production (78, 79) or methanation (45, 80, 81), there has been little effort made to investigate liquid hydrocarbon production. Karn, Shultz, and Anderson (77) used a commercial 0.5% Ru/Al_2O_3 Engelhard catalyst, 0.3 cm pellet size, to study the FT reaction in a 1.38 cm internal diameter reactor. In our study we used a 1% Ru/Al_2O_3 Engelhard catalyst, powdered to about 0.02 cm particle size, in a 0.77 cm internal diameter reactor. Our conditions were selected to ensure that problems of internal diffusion and radial temperature gradients were minimized. Let us compare the results of Karn et al. (77) which have been summarized in Figure 3.20 with those obtained by us (Table 3.42 and Figure 3.19).

Though Karn et al. (77) obtained good conversion to liquid products, C_5 to C_{20}, they also obtained large quantities of soft and hard wax. Depending whether the H_2/CO ratio was 1 or 2, the wax formation corresponded to about 45% or 35% respectively of the hydrocarbons formed. Though we worked at a lower space-velocity, 200 V/V/h, we did not observe any significant amount of wax formation even at high pressures of 3.1 MPa. For example, at experimental conditions corresponding to 3.1 MPa pressure, 240°C reaction temperature, and a H_2/CO ratio of 2, we obtained a selectivity of 95+% to C_5-C_{20} hydrocarbons. Generally, our results showed that there was a tendency to form a lower molecular weight product than that obtained by Karn et al. (77). But more importantly, it was shown in both studies that a small amount of Ru, $\leq$ 1.0% by wt, supported on alumina was active for liquid hydrocarbon production.

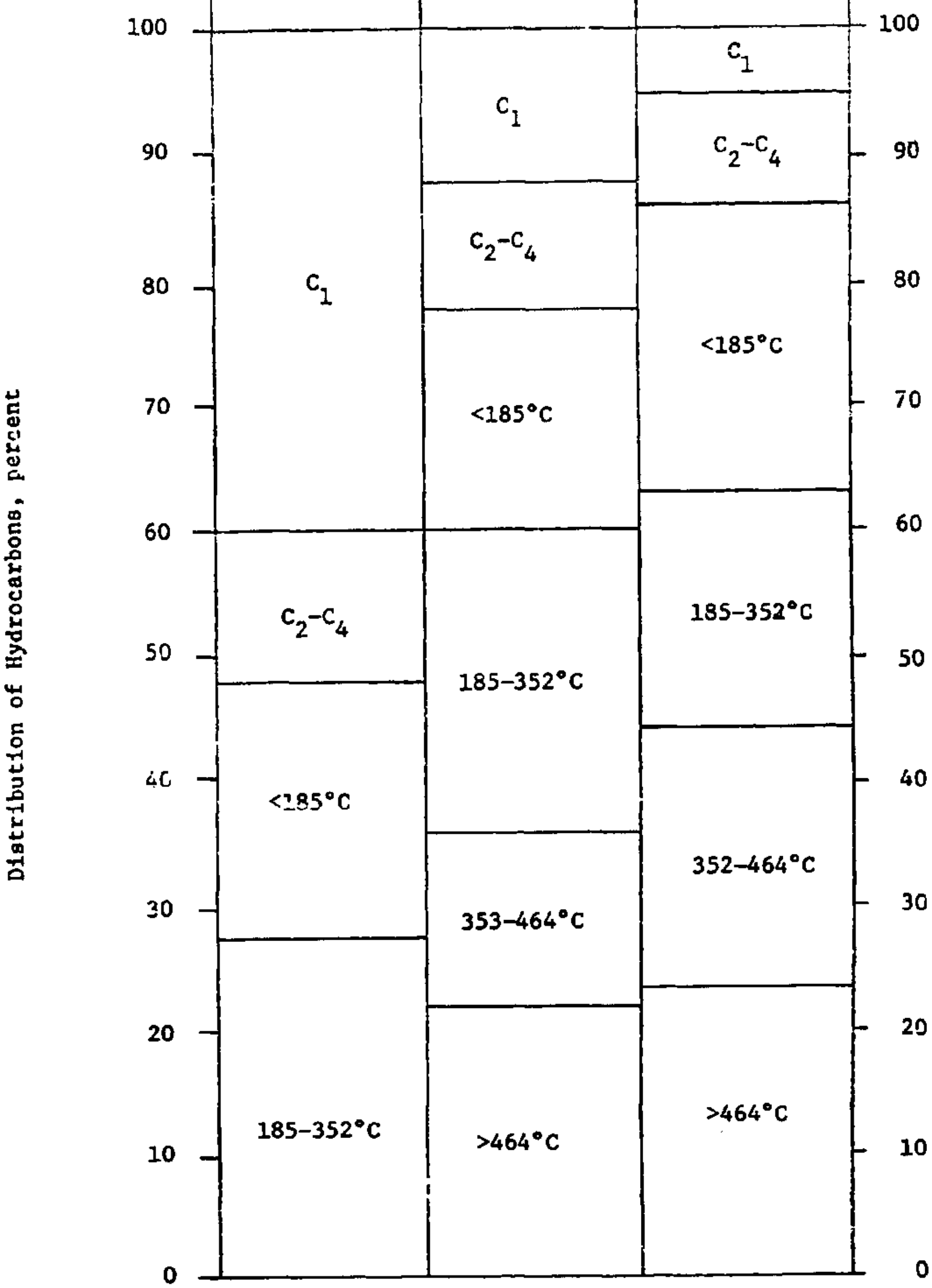
3.6.4 Summary

- Addition of either sulfur or alkali to the 1% Ru/Al_2O_3 catalyst reduced its activity considerably. However, on increasing the reaction pressure from 2.2 MPa to 3.1 MPa, a dramatic improvement of the activity of the poisoned catalyst was observed.

Figure 3.20 USBM Results with 0.5% Ru/Al_2O_3 (77)

P = 2.2 MPa, SV = 300 V/V/h

H_2/CO	3	2	1
Temperature, °C	222	225	239
Conversion, %	77	66	40



- At 240°C, both sulfided and unsulfided, alkalized Ru/Al_2O_3 catalysts showed similar activities. The presence of alkali seemed to prevent any further large deactivation by sulfur. At temperatures equal to or greater than 300°C and at a high pressure of 3.1 MPa, the unsulfided alkalized catalyst, RuK-R, did not behave as if it was poisoned and showed as high an activity as the unalkalized Ru-R catalyst.

- Alkalized and sulfided Ru catalysts generally gave a high selectivity to condensed products even at experimental conditions during which the Ru-R catalyst gave large amounts of gaseous products.

- For the Ru-R catalyst, a H_2/CO ratio is 1 gave poor activity, but good selectivity to liquid hydrocarbons; a ratio of 3, on the other hand, gave a high activity but poor selectivity. Both high activity and good selectivity were observed at a H_2/CO ratio of 2.

- The best experimental conditions at which the Ru-R catalyst showed a H_2 + CO conversion of 95%, with a selectivity to condensed products being 99%, were as follows: temperature = 240°C, pressure = 3.1 MPa, space-velocity = 200 V/V/h, and H_2/CO = 2. There was negligible wax production; 99 wt % of the condensed products being from C_5 to C_{25} hydrocarbons.

- Gaseous olefin/paraffin ratios were larger for the Ru-S2 catalyst than the Ru-R catalyst. It was interesting to note that the Ru-S2 catalyst generally produced more iso-butene than any other C_4 olefin. This was never the case with the Ru-R catalyst.

- Operation at 350°C deactivated the Ru-R catalyst probably due to coke formation. Overnight treatment in flowing H_2 at 350°C tended to restore both the catalytic activity and selectivity.

- Compared to all catalysts tested by us, the Ru-R catalyst gave the most efficient conversion of CO to liquid hydrocarbons which were mainly n-paraffins.