3.3.2 Experiments Performed

Before discussing the complete run, let us list the experiments in the order that they were performed. 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 3.19

Experimental Conditions[1] for Run 6

Experiment	H_2/CO	SV, V/V/h	T,°C	P, kPa	Time, h
6-1	2.10	200	300	1500	5.2
6-2	2.03	200	350	1500	3.8
6-3	2.27	200	350	2400	4.0
6-4	1.96	200	350	2000	4.1
6-5	2.08	200	375	2000	4.5
6-6	2.14	200	350	1000	4.7
6-7	2.03	145	350	2000	4.3
6-8	1.41	200	350	2000	4.5
6-9	3.00	200	350	2000	3.8
6-10	3.96	200	350	2000	3.7
6-11	3.38	200	400	2000	3.6
6-12	2.99	500	350	2000	6.3

3.3.3 Results and Discussion

Experiment 6-1 was performed at 302°C. This was the lowest temperature used in the run. The total H_2 + CO conversion for all the catalysts was between 40 and 46% with the lowest conversion shown by catalyst CMK-S (Table 3.20). The formation of CH_4 was significantly lower for the alkali promoted catalysts. Addition of sulfur to the CMK catalyst further lowered CH_4 and CO_2 formation. A similar trend was present with the CM catalysts. The largest amount of C_2 hydrocarbons was produced by CM-S. The highest LPG (C_3 + C_4) fraction was obtained on the unsulfided CM-R and CMK-R catalysts. The olefinic content of the gases was small, but catalyst CM-RS produced much more propylene than the others. The most significant result was that the CMK series and especially the sulfided CMK catalysts produced more C_5+ hydrocarbons than the CM series. Sulfiding the catalysts enhanced C_5+ hydrocarbon formation.

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[1] Accurate experimental conditions for each reactor and detailed results are given in the tables for run 6 in Appendix D, pages 155 to 179.

Table 3.20

Results at a Low Temperature and Intermediate Pressure Cobalt-Molybdenum Catalysts

T = 302°C, P = 1500 kPa, SV = 200 V/V/h, H_2/CO = 2.1

Catalyst	CM-R	CM-RS	CM-S	CMK-R	CMK-RS	CMK-S
Total conv., %	43.3	47.9	41.7	45.5	44.9	40.5
Selectivity, % CO conv. to:						
CO_2	50.3	38.2	42.9	41.2	29.4	29.8
CH_4	26.2	22.8	21.9	14.9	12.9	10.6
$C_2H_6 + C_2H_4$	17.5	16.9	23.4	15.2	10.9	15.1
LPG	10.4	3.2	5.7	9.5	5.5	6.3
C_5+	0+	18.9	5.9	19.2	41.2	38.2

Experiments were carried out at a higher temperature (350°C) and three different pressures: 1000, 1500 and 2000 kPa (Experiments 6-6, 6-2 and 6-4). Compared to the experiment at 300°C, smaller amounts of C_5+ hydrocarbons were formed. Catalyst CMK-RS formed C_5+ products at all three pressures, whereas CMK-S formed them significantly only at 2000 kPa. At the higher temperature the selectivity to CO_2 and CH_4 was increased for all the catalysts at all three pressures. Again alkali containing catalysts produced the least amount of CH_4. At all three pressures, catalyst CM-S again produced the largest amount of C_2 hydrocarbons. The formation of olefins decreased as the pressure was increased, and catalyst CMK-RS gave the largest amount of olefins, especially propylene. Table 3.21 indicates the trend of propylene formation.

Table 3.21

Propylene Formation at Low Pressure Cobalt-Molybdenum Catalysts

T = 350°C, P = 1000 kPa, SV = 200 V/V/h, H_2/CO = 2.14

CM Series	% CO to C_3H_6	CMK Series	% CO to C_3H_6
CM-R	0.034	CMK-R	0.115
CM-RS	0.075	CMK-RS	0.225
CM-S	0.028	CMK-S	0.05

Two interesting points can be noted from the above table; (a) addition of alkali increases propylene formation, and (b) in both series the reduced catalyst with nominally 1% by wt S gives more C_3H_6 than the corresponding reduced or fully sulfided catalyst. The latter catalyst gives the least C_3H_6. If olefins are the primary products in the FT reaction then fully sulfided, unalkalized catalysts have the highest olefin hydrogenation capacity.

Another important trend, for LPG production, can be seen in Table 3.22.

Table 3.22

LPG Formation
Cobalt-Molybdenum Catalysts

T = 350°C, SV = 200 V/V/h, H_2/CO = 2.0

Catalyst	Pressure	% CO Converted to $C_3 + C_4$ hydrocarbons		
		1000 kPa	1500 kPa	2000 kPa
CM Series				
CM-R		5.27	6.46	5.81
CM-RS		1.9	0.94	0.43
CM-S		2.0	1.95	2.97
CMK Series				
CMK-R		8.40	10.19	9.84
CMK-RS		4.94	4.98	3.83
CMK-S		7.66	6.82	7.22

The addition of alkali promoter and the type of catalyst pretreatment are both important for LPG formation. In both catalyst series the dependence of LPG formation on catalyst pretreatment was as follows:

Reduced > calcined and fully sulfided > Reduced and partially sulfided

For similar pretreatments the alkali promoted catalysts gave more LPG; in fact for LPG production CMK-S > CM-R. The effect of pressure was nominal compared to the effect of alkali promotion and pretreatment.

The highest pressure used in Run 6 was 2500 kPa in Experiment 6-3. However, this experiment in which the average H_2/CO ratio was 2.3 will not be compared specifically to the experiments discussed above. It can be seen that all the trends are similar to those noted for Experiment 6-4, with one important exception. The value of the selectivity to C_5+ hydrocarbons is significantly enhanced at the high pressure of 2500 kPa; it is, however, not as large as that obtained at a lower temperature i.e., in Experiment 6-1, which was conducted at a lower pressure (1500 kPa).

It can be inferred from Experiments 6-1, 6-3, and 6-4 that catalysts CMK-RS and CMK-S are most effective for the production of C_5+ hydrocarbons at low temperatures (≤ 300°C) and high pressures (> 2000 kPa).

Let us now discuss the effect of H_2/CO ratios. The ratios were varied as follows: 1.41, 1.96, 3.00, and 3.96 in Experiments 6-8, 6-4, 6-9, and 6-10 respectively. Figure 3.13 indicates the activity of the various catalysts. The activity of all the catalysts fell as the H_2/CO ratio was increased. The most rapid decrease was observed between the H_2/CO ratios of 3 and 4. Catalyst CM-S was most active, and CM-RS was the next most active catalyst. This shows that sulfiding a non-alkalized catalyst improved the activity, whereas sulfiding an alkali promoted catalyst did not change the activity significantly. First, we will compare the important aspect of C_5+ hydrocarbon production.

Table 3.23

The Effect of H_2/CO Ratio on C_5+ Hydrocarbon Formation
Cobalt-Molybdenum Catalysts

T = 350°C, P = 2000 kPa, SV = 200 V/V/h

Catalyst		% CO Converted to C_5+ Hydrocarbons			
	H_2/CO	1.41	1.96	3.00	3.96
CM Series					
CM-R		7.8	0+	7.5	0+
CM-RS		3.1	7.6	7.3	0+
CM-S		0+	0+	0+	0+
CMK Series					
CMK-R		11.3	0+	9.2	0+
CMK-RS		22.5	9.7	18.9	0.2
CMK-S		9.8	13.8	17.3	0+

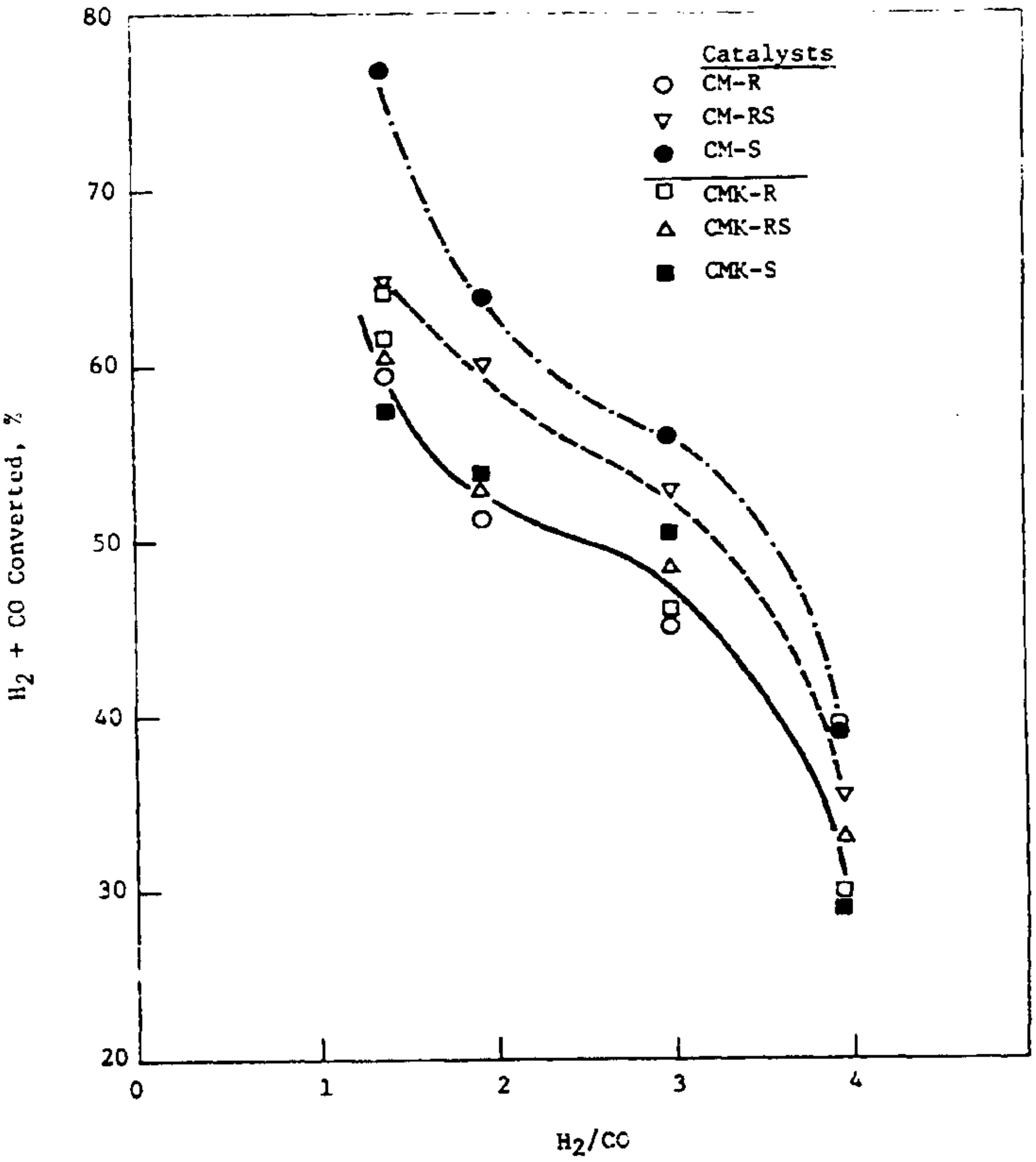
As noted before (Section 2.4) the accuracy of C_5+ selectivity values below 10% is not good. However, from the trends seen in Table 3.23 several important conclusions can be made. First, $H_2/CO \leq 3$ is necessary for C_5+ hydrocarbon formation. Secondly, alkali promoted catalysts, especially CMK-RS and CMK-S catalysts, markedly favor C_5+ production. Finally, CM-S is the worst catalyst for the production of condensed products. Due to the inaccuracies of individual low selectivities we will not compare the detailed effect of the H_2/CO ratios between 1.41 and 3.0.

Though CM-S is the worst catalyst for C_5+ production, it is the best catalyst for CH_4 and C_2 hydrocarbon formation at all H_2/CO ratios.

Figure 3.13

Dependence of Activity on the H_2/CO Ratio
Cobalt-Molybdenum Catalysts

T = 350°C, P = 2000 kPa, SV = 200 V/V/h



The production of C_2 hydrocarbons seems to be dependent on the catalyst pretreatment, and the trend is independent of the H_2/CO ratio:

CM-S > CMK-S ≥ CMK-R > CM-R ≥ CM-RS > CMK-RS

The fully sulfided catalysts produce more C_2 hydrocarbons than the corresponding catalysts which were reduced and partially sulfided. Methane production, on the other hand, is more dependent on the promoter rather than the catalyst pretreatment and is always less for the CMK Series.

Olefin production (C_3H_6 and $C_4^=$) is very small, and it is most evident only at $H_2/CO = 1.41$. Once again the promoter and the catalyst pretreatment are both important. The order for olefin selectivity is as follows:

CMK-RS > CMK-R > CMK-S ≥ CM-R > CM-RS > CM-S

In both series the fully sulfided catalysts are least active for olefin formation. It can be inferred that (a) fully sulfiding a calcined catalyst enhances, and (b) the addition of alkali lowers, the olefin hydrogenation capacity of the catalyst.

Finally, let us tabulate the formation of LPG at various H_2/CO ratios.

Table 3.24

LPG Formation
Cobalt-Molybdenum Catalysts

$T = 350°C$, $P = 2000$ kPa, $SV = 200$ V/V/h

Catalyst		% CO Converted to $C_3 + C_4$ Hydrocarbons			
	H_2/CO	1.41	1.96	3.00	3.96
CM Series					
CM-R		4.05	5.81	2.58	3.29
CM-RS		0.57	0.43	0.27	0.24
CM-S		5.25	2.97	2.71	1.87
CMK Series					
CMK-R		8.53	9.84	5.74	4.65
CMK-RS		4.23	3.83	2.61	1.91
CMK-S		9.27	7.22	5.12	5.44

The general trend shows a decrease in LPG formation as the H_2/CO ratio is increased. When comparing catalysts with similar pretreatments, alkali promoted catalysts always give more $C_3 + C_4$ hydrocarbons i.e.,

CMK-R > CM-R   CMK-RS > CM-RS   CMK-S > CM-S

Catalysts CMK-R and CMK-S produce most LPG. One interesting trend, similar to the one seen in Table 3.22, is that for both catalyst series, reducing and then partially sulfiding a catalyst is the pretreatment that causes the smallest production of LPG. However, fully sulfiding a calcined catalyst gives LPG values similar to the reduced unsulfided catalyst.

Experiment 6-11 was carried out at 400°C to check if any of the catalysts could be used for SNG production. Catalysts CM-RS and CM-S gave a total H_2 + CO conversion of 55% and showed CH_4 selectivities (i.e. % CO converted to CH_4) of 64% and 68% respectively. Alkalized catalysts showed lower activities and lower selectivity to CH_4. It is possible that a cobalt-molybdenum catalyst, resistant to sulfur poisoning, could be used for the production of SNG. Higher space velocities than 200 V/V/h could be used, and the corresponding lower conversion could be compensated by re-cycling the unused reactants. Raney nickel or other nickel catalysts are very active for methanation but they require sophisticated sulfur-guard systems to prevent deactivation of the catalyst by sulfur. Cobalt-molybdenum catalysts, though not as active as nickel catalysts, are significantly more sulfur resistant and hence, in this case, one could dispense with expensive sulfur removal systems.

In all experiments more iso-butane was formed than the corresponding C_4 olefins. This is different from the observations on cobalt and iron FT catalysts. When C_4 olefins were observed, the amounts of iso-butene and 2-butene were approximately the same as, and sometimes more than, 1-butene. The values (< 0.5 μ moles) were too small for quantitative comparison. This result, too, is different from cobalt and iron catalysts where 1-butene was the predominant C_4 olefin. Alkali promoted catalysts usually gave the most iso-C_4H_{10}. An example of the selectivity and trend of iso-C_4H_{10} formation, compared to n-C_4H_{10} and C_4H_8 formation, can be seen in Table 3.25.

Table 3.25

Iso-butane Formation
Cobalt-Molybdenum Catalysts

T = 350°C, P = 2000 kPa, SV = 200 V/V/h, H_2/CO = 1.41

Catalyst	% CO converted to:	Iso-C_4H_{10}	n-C_4H_{10}	C_4H_8
CM-Series				
CM-R		0.12	0.75	0+
CM-RS		0.01	0.04	0+
CM-S		0.10	0.44	0+
CMK Series				
CMK-R		0.30	1.77	0.20
CMK-RS		0.15	0.58	0.18
CMK-S		0.39	1.77	0+

Carbon number distributions are shown in Figures 3.14, 3.15, and 3.16. Figure 3.14 compares CMK-R and CMK-S catalysts. The CMK-R catalyst showed a maximum at C_{14}-C_{15}, and the distribution was quite normal. The sulfided CMK-S catalyst showed a much lower maximum at C_{17}, and then the shape deviated completely from the curve for the reduced, unsulfided CMK-R catalyst. The sulfided catalyst showed a broad distribution of C_{25} to C_{40} hydrocarbons. Figure 3.15 compares the CM-RS and CM-S catalysts; a maximum is observed at C_{16}-C_{17} and the trend of heavy hydrocarbons is similar to the CMK-S catalyst curve in Figure 3.14. Finally, Figure 3.16 compares the unsulfided promoted and unpromoted catalysts, CM-R and CMK-R; the maximum is around C_{14}-C_{15} and the shape and distribution is very similar. It can be inferred that (a) though addition of alkali increases the amount of condensed products formed, the overall distribution is unaffected by the alkali promoter, (b) the distribution is significantly changed by the addition of sulfur to either a CM or a CMK catalyst, and the change is similar for both types of catalyst and (c) sulfur increases the molecular weight of the products.

A gas chromatograph-mass spectrometric analysis was performed on the condensed product obtained with a CMK-R catalyst. In each carbon number group the n-paraffin was the major product; iso-paraffins and alkenes were also present. Small quantities of alkyl benzenes were also observed. In Table 3.26 a breakdown of the materials has been attempted; after C_{12}, a combined percentage of non-n-paraffins is given.

It is interesting to note the systematic formation of alkyl benzenes (Table 3.26). In the chromatograph results corresponding to heavy hydrocarbons ($> C_{17}$) mass spectrometric fragments denote the presence of heavy alkyl benzenes and substituted phenanthrenes. However, weak column resolution, and the fact that the amount of the aromatic compounds is small prevented the identification of individual aromatics. The maximum aromatic content is about 10% by wt. The total amount of n-paraffins in the product is approximately 70% by wt. The rest of the material is iso-paraffinic and olefinic; the former is estimated to be more than the latter.

Our results indicate that both the oxidic and sulfidic forms of cobalt-molybdenum catalyst are active for CO hydrogenation. The selectivity, however, is very dependent on catalyst pretreatment and the presence of alkali. Let us now discuss some important aspects of alumina supported cobalt-molybdenum catalysts.

Recently Ratnasamy and coworkers (63) showed that the presence of small quantities of sodium in the Al_2O_3 support affected the reducibility of the catalyst. They proposed that when Na ions were present cobalt occurred chiefly as Co_3O_4 rather than dispersed Co^{2+} ions. The cobalt oxide was easily reduced in H_2 to the metal which in turn accelerated the reduction of Mo(VI) to Mo(V) and Mo(IV). In the absence of sodium in the support cobalt was predominantly in a Co^{2+} state which was irreducible in H_2, and consequently though the reduction of Mo(VI) did take place it was not enhanced. Using unalkalized Al_2O_3 supports, Patterson et al. (64) also noted that the cobalt in their unreduced Co-Mo/Al_2O_3 catalyst underwent little change in pure H_2 at 500°C. They found that after reduction the mole fractions of surface Mo(VI), Mo(V), and Mo(IV) were about 0.25, 0.35, and 0.4 respectively. In our catalysts the alkali was impregnated on the catalyst after it had been made and calcined. Hence, the presence of alkali in our catalyst may not

Figure 3.14

Distribution of Condensed Products
Cobalt-Molybdenum Catalysts

T = 350°C, P = 2000 kPa, SV ≈ 150 V/V/h, H_2/CO = 2.0

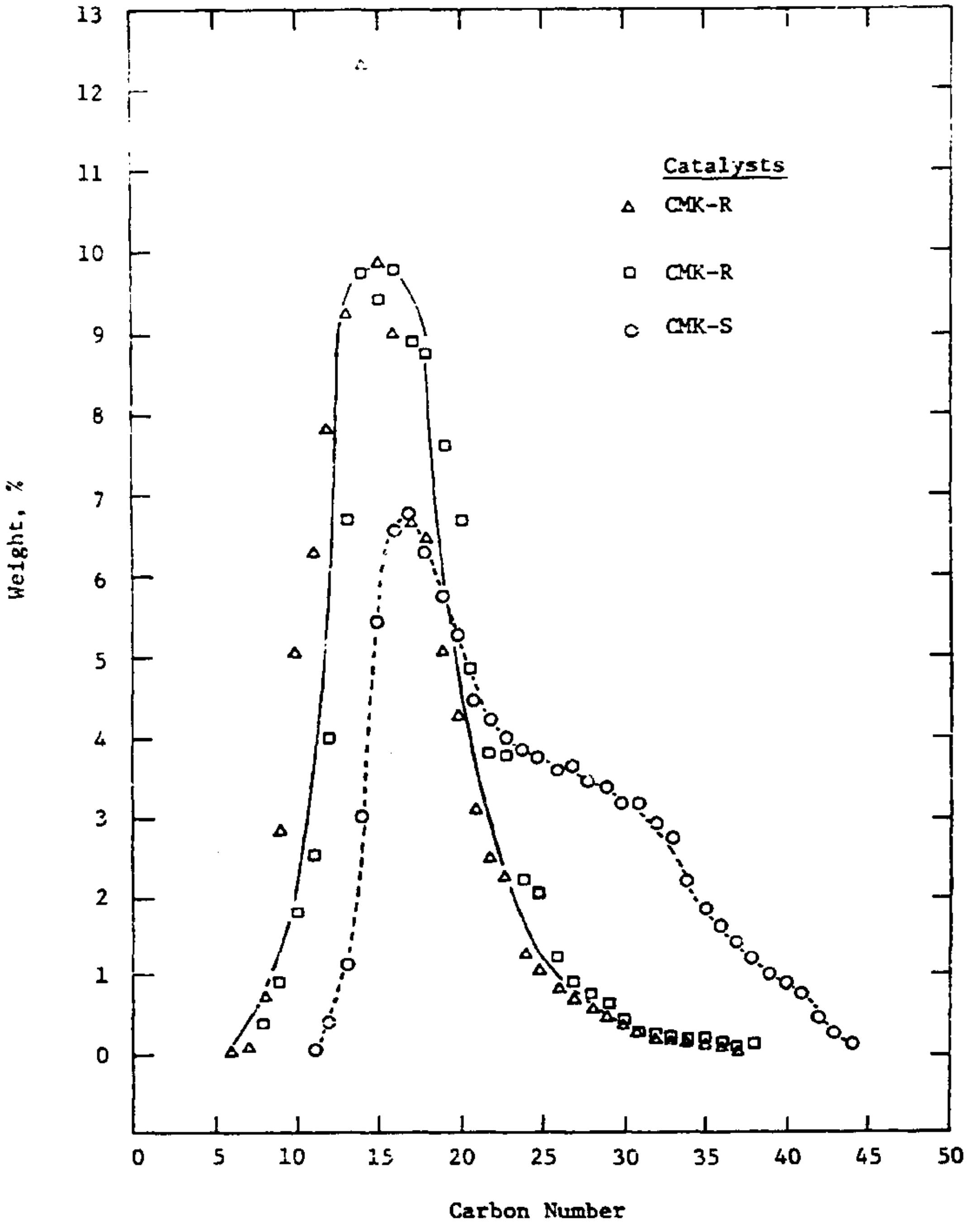


Figure 3.15

Distribution of Condensed Products
Cobalt-Molybdenum Catalysts

T = 350°C, P = 2000 kPa, SV = 150 V/V/h, H_2/CO = 2.0

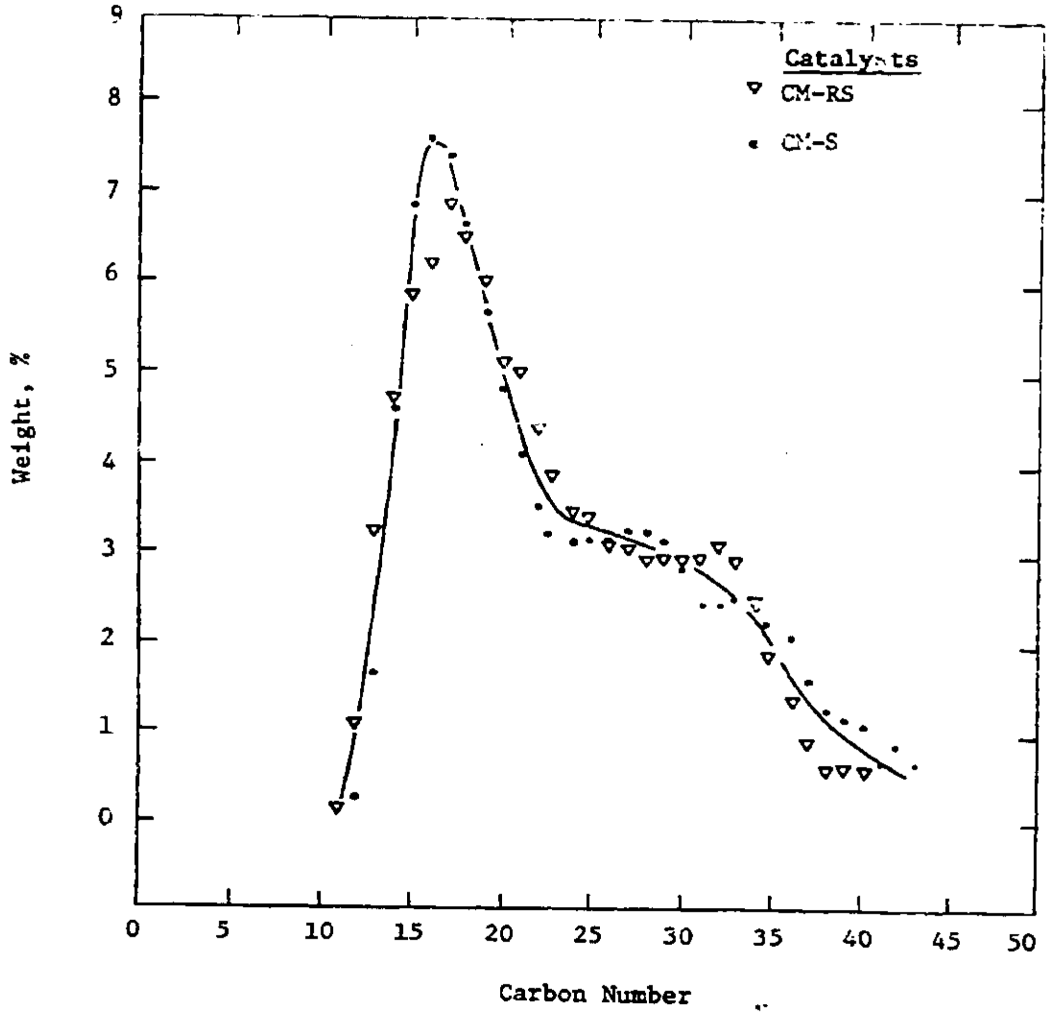


Figure 3.16

Distribution of Condensed Products
Cobalt-Molybdenum Catalysts

T = 350°C, P = 2000 kPa, SV = 200 V/V/h, H_2/CO = 1.41

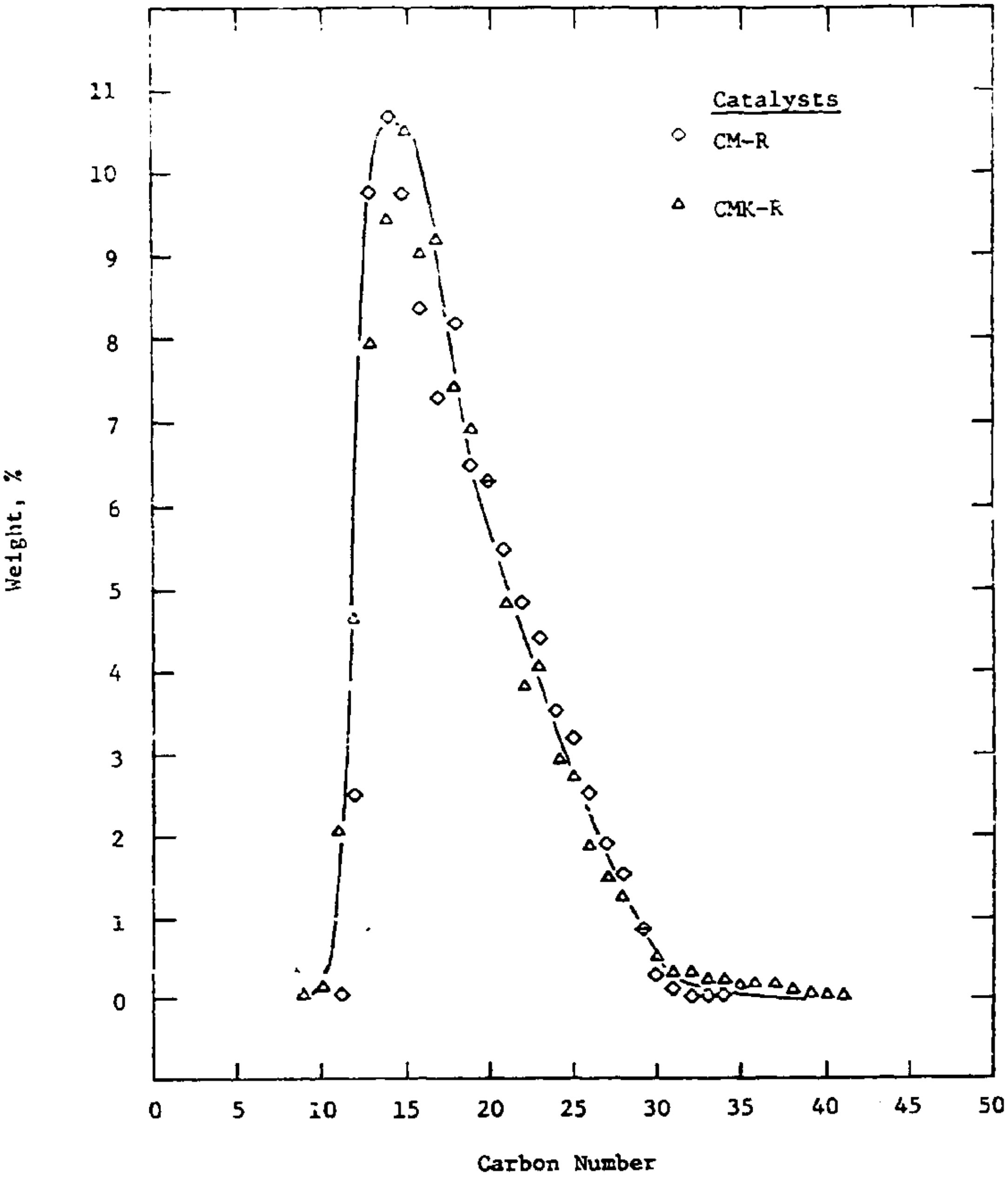


Table 3. 26

Components in Condensed Product
Reduced, Alkalized, Cobalt-Molybdenum Catalyst

T = 350°C, P = 2000 kPa, SV = 150 V/V/h, $H_2/CO = 2$

Carbon number[3]	Total weight%	Component %			Aromatics[2]
		n-paraffin	iso-paraffin[1]	olefins[1]	
C_8	0.76	89.4	5.3	5.3	ϕC_1
C_9	2.85	83.9	10.5	5.6	ϕC_2
C_{10}	5.07	81.9	13.2	4.9	ϕC_3
C_{11}	6.32	81.9	13.3	4.8	ϕC_4
C_{12}	7.84	75.5	16.7	7.8	ϕC_5
C_{13}	9.25	71.4	28.6		ϕC_6
C_{14}	12.32	53.1	46.9		$\phi - \phi + \phi C_7$
C_{15}	9.93	65.2	34.8		ϕC_8
C_{16}	9.00	68.0	32.0		ϕC_9
C_{17}	6.67	77.1	22.9		
C_{18}	6.49	64.4	35.6		
C_{19}	5.06	71.1	28.9		
C_{20}	4.28	71.7	28.2		
C_{21}	3.12	81.8	18.9		
C_{22}	2.50	84.8	15.2		

[1] The values of iso-paraffins and olefins are not accurate due to poor chromatographic resolution and also due to the fact that aromatic chromatograph peaks coincide with the non-normal paraffin aliphatic peaks. Values of n-paraffins are accurate.

[2] Aromatics are mostly alkyl benzenes (ϕC_n); bi-phenyl ($\phi - \phi$) was also observed. The carbon grouping on the benzene ring is not known. Aromatics heavier than ϕC_9 do exist (see Discussion).

[3] 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 more inaccurate.

influence reduction in the same way as discussed by Ratnasamy et al. (63). But besides the possibility of influencing catalytic reduction, alkali may interact with the cobalt and molybdenum species in a way similar to the "synergy by contact" hypothesis put forward by Hagenbach et al. (65) and Canesson et al. (66). Finally, the alkali could also affect the sulfidation of the cobalt and molybdenum species in our catalyst.

It has been found that during sulfidation Co-Mo/Al_2O_3 catalysts do not sulfide completely (64, 67), and pre-reduced samples do not sulfide to as great an extent as calcined, unreduced catalysts (64, 68). However, as the sulfided catalyst has sufficient sulfur (69) an extensive destruction of the oxide monolayer probably occurs with cations embedded in the γ-Al_2O_3 support diffusing back to the surface (69). The structure of the sulfide catalyst, intercalated (70, 71) or otherwise (72), may therefore be quite different from the structure of the precursor oxidic catalyst (72). But it is important to note that though the oxidic and sulfidic catalyst structures may be different they both provide the required sites for the activation of CO and H_2, sites which are probably not metallic in nature. As mentioned before, though conversion levels are close on the differently treated Co-Mo catalysts used by us, the selectivity patterns are different. An important difference in selectivity is that alkalized catalysts form less methane but form heavier hydrocarbons than alkali-free catalysts. Furthermore, the presence of sulfur enhances the molecular weight of condensed hydrocarbons (Figures 3.14, 3.15, 3.16).

The FT reaction on oxidic or sulfidic Co-Mo/Al_2O_3 catalysts involves hydrocarbon chain growth on a non-metallic catalyst, and may thus be akin to polymerization of $TiCl_3$ as proposed by Cossee and Arlman (73). In bulk $TiCl_3$ the Ti^{3+} is octahedially surrounded by Cl^- ions. On the surface one octahedral co-ordination site may be empty (anionic vacancy), and Cl^- ion adjacent to this vacancy is exchanged with $Al(C_2H_5)_3$ to form an alkyl ligand. This coordinatively unsaturated surface site is capable of adding a monomer ligand. The monomer unit is then incorporated via insertion into the adjacent alkyl group, and the anionic vacancy is regenerated. A new monomer ligand is formed, and this growth process continues till the chain is terminated with H_2.

The growth of hydrocarbon chains on oxidic and sulfidic Co-Mo/Al_2O_3 catalysts may be explained in a way similar to the Cossee-Arlman model for polymerization. Let us assume that an active site responsible for CO conversion and hydrocarbon growth must contain adjacent anionic vacancies. The activity of the catalyst will then depend on the number of available surface anionic vacancies. The growth of the molecule, and hence the selectivity, will depend on the interaction of the reaction intermediate, formed at a vacancy, with the site which in turn will be influenced by its environment which may or may not contain sulfur or alkali. For example, the site environment may determine the strength of the intermediate ligand, the incorporation of other intermediates for the chain to grow, or the curtailment or acceleration of chain termination processes. One must explain, however, why unalkalized catalyst CM-S, which has the best selectivity for CH_4 and C_2 hydrocarbon formation and the poorest selectivity for C_5+ hydrocarbon formation, gives heavier molecular weight condensed products than unsulfided CM-R or CMK-R catalysts (Figures 3.14, 3.15, 3.16). The proposed mechanism may still be valid if we postulate that the site environment is crucial to the size of the hydrocarbons formed. For example, in catalyst CM-S, most of the sites have an environment which promotes CH_4 and C_2 hydrocarbon formation, however a few sites, probably influenced by sulfur, are present to give small quantities of very heavy (C_{30}+) hydrocarbons. In alkalized catalysts the site environments will be different leading to less CH_4 formation. Furthermore, in all cases it is possible that H_2O will be competitively adsorbed on hydrocarbon formation sites to give CO_2 via the shift reaction.

3.3.4 Summary

Table 3.27 summarizes the effectiveness of Co-Mo/Al_2O_3 promoted and pretreated in different ways for the formation of various hydrocarbon products.

Table 3.27

Selectivity Trends on Co-Mo/Al_2O_3 Catalysts

	Best Catalyst	Worst Catalyst
C_5+ products	CMK-RS, CMK-S	CM-S
LPG	CMK-R, CMK-S	CM-RS
$C_2H_6 + C_2H_4$	CM-S	CM-RS, CMK-RS
CH_4	CM-S, CM-RS	CMK-S, CMK-RS

- Condensed hydrocarbons were obtained with Co-Mo/Al_2O_3 catalysts, and addition of sulfur to the alkali-promoted catalyst enhanced this selectivity considerably. This could mean that an alkali-sulfur interaction takes place which is beneficial for the formation of heavy hydrocarbons. It should be further noted that catalyst CMK-RS generally gave higher yields of C_5+ products than the CMK-S catalyst, indicating that besides catalyst promotion the type of pretreatment may also be important. High pressure (> 2000 kPa) and low temperatures ($\lesssim$ 300°C) favor condensed hydrocarbon production.

- The distribution of the condensed products was not dependent on the alkali promoter. However, addition of sulfur for both promoted and unpromoted catalysts changed the distribution drastically, with larger quantities of C_{25} to C_{40} hydrocarbons being produced.

- The major fraction of the hydrocarbon product was normal paraffin. Iso-paraffins were also present and were more abundant than the corresponding alkenes (normal or branched). A qualitative observation revealed that there seemed to be more internal olefins rather than α-olefins present. Small amounts of alkyl benzenes and other aromatic compounds were also observed.

- Methane was the principal hydrocarbon produced by all the catalysts. Unalkalized catalysts, and especially CM-RS and CM-S, were the most active for methane production. These types of catalysts may be useful as sulfur resistant methanation catalysts. Addition of alkali to a catalyst significantly reduced its propensity for methane formation.

- When either catalyst CM or CMK was first reduced and then sulfided it showed poor selectivity for C_2, C_3, and C_4 hydrocarbons. But if the catalysts were calcined and fully sulfided the selectivity for these hydrocarbons was increased. This proves that, besides addition of promoters, catalyst selectivity may be influenced by adopting special pre-treatment procedures.

- The amount of olefins produced was very small. From the results on the gaseous products it was seen that alkali enhanced the olefin content in the products. Catalyst CMK-RS produced the most amount of olefin, especially propylene. Fully sulfiding a catalyst. i.e. CMK-S or CM-S, reduced the amount of olefin observed. If olefins are the primary products in the reaction, addition of alkali decreases and full sulfidation increases the hydrogenation capacity of a cobalt-molybdenum catalyst.

3.4 Molybdenum Disulfide Promoted with KOH

3.4.1 Catalyst Pre-treatment

The MoS_2 was obtained commercially from Climax Molybdenum as a technical grade reagent and impregnated with 3% KOH at Harshaw Chemical Company. The BET surface are of the catalyst was 2.16 m^2/g. The catalyst was a fine powder, and 50 cm^3 (75.5 g) of it was loaded into a reactor. The reactor, after being assembled on the unit, was first flushed and then pressure tested with He. The pressure was then reduced to atmospheric pressure, and the temperature was then raised to 450°C, in 50°C increments, under flowing hydrogen. The H_2 space-velocity was 720 V/V/h, and the H_2 pre-treatment at 450°C was continued for 23 h. The reactor was then flushed with He.

3.4.2 Experiments Performed

The list of experiments in the order that they were performed is given in Table 3.28. After each experiment the catalyst was kept overnight in flowing He at the same temperature and pressure used in the experiment.

Table 3.28

Experimental Conditions[1] for Run 7

Experiment	H_2/CO	SV, V/V/h	T, °C	P, kPa	Time, h
7-1	1.97	179	353	2050	4.9
7-7	1.09	99	351	2050	5.1
7-8	1.98	102	350	2050	5.0
7-9	2.99	207	400	2050	18.1

3.4.3 Results and Discussion

A typical example of the catalytic behavior of MoS_2 promoted with KOH for the FT synthesis is given in Table 3.29. The reaction rate at the conditions given in Table 3.29 for the conversion of CO was 1.2×10^{-7} mol $m^{-2}s^{-1}$. Assuming a site density of 10^{19} sites/m^2, the corresponding turnover number N_{CO} is $7.2 \times 10^{-3} s^{-1}$ at 353°C and 2050 kPa.

The catalyst showed good selectivity for the formation of condensed products with little CO_2 or hydrocarbon gas production. And approximately equal amounts of gaseous olefins and paraffins were usually formed. It may tentatively be inferred that the activity was enhanced at low H_2/CO ratios.

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[1] NOTE: Most of Run 7 consisted of tests on the W-based catalysts which will be described later. The MoS_2 + KOH catalyst was used in reactor 4. Detailed results are given in the tables for Run 7 in Appendix D, pages 182 to 200.

Table 3.29

Fischer-Tropsch Synthesis on MoS_2 + 3% KOH

T = 353°C, P = 2050 kPa, SV = 179 V/V/h, H_2/CO = 1.97

CO_2-free contraction, %	49.29
H_2 conversion, %	49.03
CO conversion, %	55.37
Total H_2 + CO conversion, %	51.61
H_2 usage ratio	0.64
Gaseous products, µmol/min	
CH_4	30.02
C_2H_6 + C_2H_4	6.32
C_3H_8	0.68
i-C_4H_{10}	1.01
n-C_4H_{10}	0.10
1-C_4H_8	0.21
i-C_4H_8	0.19
cis-2-C_4H_8	0.07
CO_2	0.09
	57.71
Selectivity, % CO converted to:	
C_5+	90.44
CH_4	2.65
CO_2	5.10
CO conv. to C_5+/CO conv. to hydc. gas	20.31

The high selectivity of alkali promoted MoS_2 to condensed products, as seen in Table 3.29, is also observed under conditions, such as high temperature and high H_2/CO ratio, which enhance methanation. Let us compare (Table 3.30a) such an experiment with a similar experiment on the alkalized, sulfided $Co-Mo/Al_2O_3$ catalyst discussed in Section 3.3.3.

Table 3.30a

Comparison of Alkalized MoS_2 and Sulfided $Co-Mo/Al_2O_3$ Catalysts

Catalyst	MoS_2	$Co-Mo/Al_2O_3$ (CMK-S)
Alkali promoter	yes	yes
Catalyst weight, g	75.5	36.1
Temperature, °C	400	398
Pressure, kPa	2050	2075
H_2/CO	3.0	3.4
Space velocity, V/V/h	207	201
Total H_2 + CO conv., %	32.6	43.9
Selectivity, % CO converted to:		
C_5+	82.3	0+
CH_4	6.8	48.6
CO_2	8.1	42.5

The Co-Mo catalyst forms mainly CH_4 and CO_2 via the shift reaction. The MoS_2 catalyst, on the other hand, even at 400°C and $H_2/CO = 3.0$, produces mainly condensed products, and the activity of the catalyst for methanation or the shift reaction is small.

Let us now compare (Table 3.30b), in detail, the same two catalysts discussed above used at experimental conditions which should favor the formation of condensed products.

The main difference in the behavior of the two catalysts may be seen in the last row of Table 3.30b; 20 times more CO is converted on MoS_2 to condensed products rather than to gaseous hydrocarbons. The Co-Mo catalyst gives much more CH_4, C_2, and LPG than MoS_2. The shift reaction is also more pronounced on the Co-Mo catalyst. This large selectivity difference between two sulfided, alkali-promoted molybdenum-based catalysts is important. The Co-Mo catalyst is also a better olefin hydrogenation catalyst as seen from the ratio of gaseous olefins and paraffins.

Table 3.30b

Comparison of Alkalized MoS_2 and Sulfided $Co\text{-}Mo/Al_2O_3$ Catalysts

Catalyst	MoS_2	$Co\text{-}Mo/Al_2O_3$ (CMK-S)
Alkali promoter	yes	yes
Catalyst weight, g	75.5	36.1
Temperature, °C	353	348
Pressure, kPa	2050	2070
H_2/CO	1.97	1.97
Space velocity, V/V/h	179	200
H_2 converted, μmol/min	1974.04	2015.69
H_2 conversion, %	49.03	45.03
CO converted, μmol/min	1131.70	1622.28
CO conversion, %	55.37	71.03
Total H_2 + CO conv., %	51.16	53.81
H_2 usage ratio	0.64	0.55
Gaseous Products, μmol/min		
CH_4	30.02	298.94
$C_2H_6 + C_2H_4$	6.32	170.92
C_3H_8	0.68	31.98
C_3H_6	1.01	0.05
$i\text{-}C_4H_{10}$	0.10	0.82
$n\text{-}C_4H_{10}$	0.20	4.43
$1\text{-}C_4H_8$	0.18	0.00
$i\text{-}C_4H_8$	0.07	0.00
$cis\text{-}2\text{-}C_4H_8$	0.09	0.00
CO_2	57.74	640.47
CO conv. to hydc. gas, μmol/min	50.38	757.96
CO converted to C_5+ hydrocarbons, μmol/min	1023.57	223.84
Selectivity, % CO converted to:		
CH_4	2.7	18.4
C_2	1.1	21.1
$C_3 + C_4$	0.7	7.2
C_5+	90.4	13.8
CO_2	5.1	39.5
CO conv. to C_5+/CO conv. to hydc. gas	20.3	0.29

Finally, Figure 3.17 gives a distribution of condensed products. This distribution is very different from that obtained with the Co-Mo catalyst (CMK-S), Figure 3.14. In the present case, the condensed products are lighter with 91 wt % of the condensed products being C_7 to C_{25} and the remaining 9 wt % of the products being C_{26} to C_{44}. Moreover, the liquid product is not mainly n-paraffinic[1] in nature. This latter result is different from that obtained with any of the catalysts tested by us. It is interesting to note that in the same experiment (Experiment 7-8) the production of C_3H_8 and n-C_4H_{10} was slightly larger than the corresponding olefins; also more n-C_4H_{10} was formed than iso-C_4H_{10}. Due to these observations it is difficult to assume that the non-paraffic part of the liquid product is either olefins or branched paraffins. As further analysis was not done we shall refrain from discussing the nature of the condensed product.

Stewart (74) who used MoS_2 promoted with KOH also obtained condensed products with CO and H_2 (Table 3.31). MoS_2 without KOH or with other promoters produced mainly CH_4. Table 3.32 gives an analysis of the condensed products via fractional distillation.

Table 3.31

The Influence of Promoters on MoS_2 Catalysts (74)

$P = 1.4$ MPa, $H_2/CO = 2$

Promoter	T, °C	SV, V/V/h	CO conv., %	% converted CO converted to C_3+ hydc. and oxygenated compounds
None	282	86	95	0
29% ThO_2	288	108	99	0
25% Cr_2O_3	282	103	97	0
30% Al_2O_3	279	107	96	0
2-3% KOH	276	183	69	30

Table 3.32

Fractional Distillation of Products Obtained with MoS_2 + 2-3% KOH (74)

Component	Mol, %
C_3	1
C_4	11
C_5	22
40-57°C	22
57-67°C	29
71-85°C	4
Above 85°C	11

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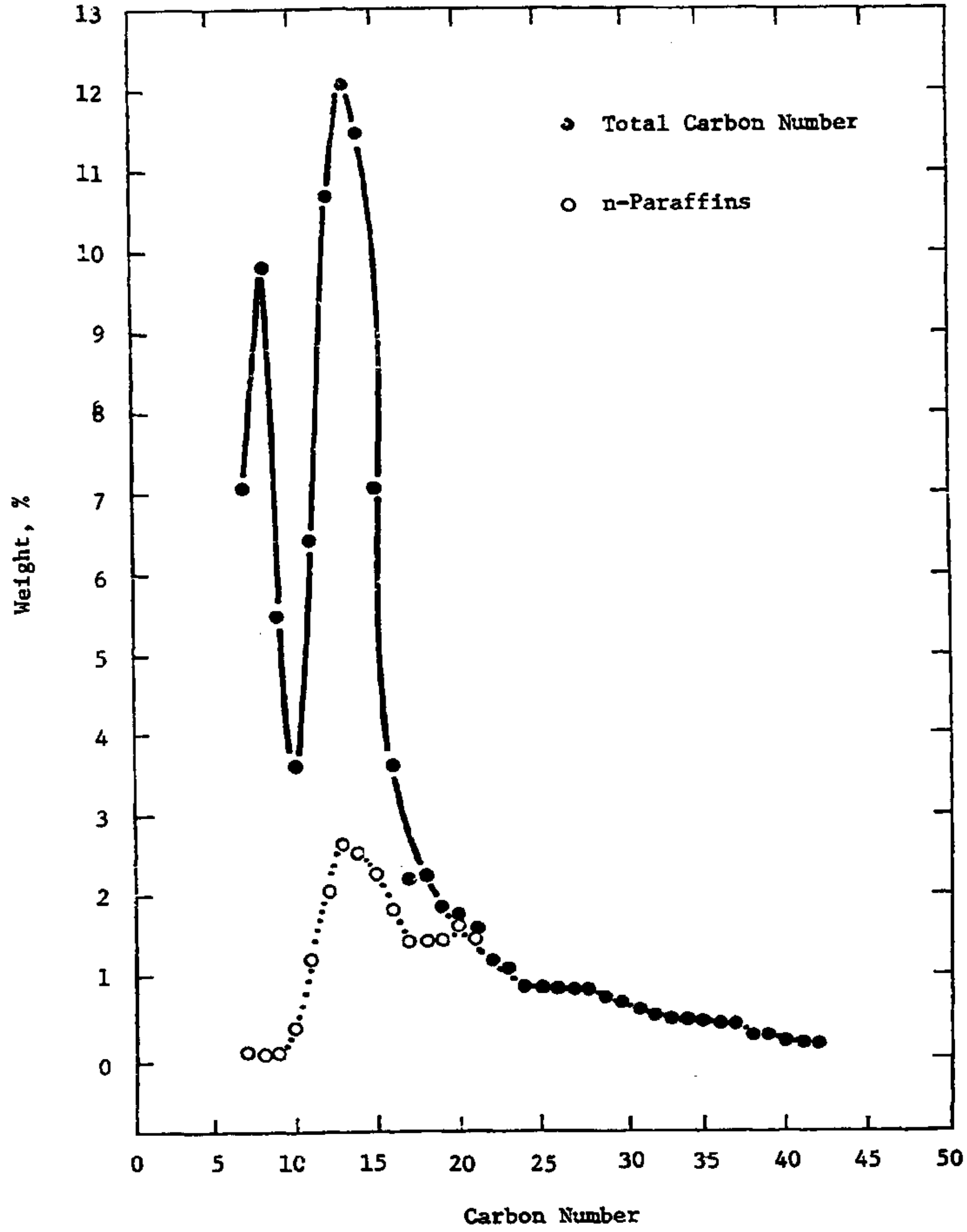
[1] After a carbon number of 20 it is difficult to differentiate between n-paraffins and other condensed products.

Figure 3.17

Distribution of Condensed Products
Catalyst: MoS_2 Promoted with KOH

T = 351°C, P = 2060 kPa, SV = 102 V/V/h, H_2/CO = 1.98



From our results and those of Stewart (74) it seems that the presence of alkali influences the formation of heavy products from CO and H_2. And as also seen in Section 3.3.3, for Co-Mo/Al_2O_3 catalysts, the alkali promoted, sulfided catalysts gave the largest conversion to condensed products. An alkali-sulfur interaction hence seems to be important for Mo-based catalysts to produce C_5+ products in the FT synthesis.

For the Co-Mo/Al_2O_3 catalysts we proposed that it was necessary to have adjacent surface anionic vacancies for H_2 + CO conversion and for hydrocarbon chain growth. The activity, i.e. the % H_2 + CO converted, was stated to be probably dependent on the number of such available vacancies. Whereas the extent of growth, i.e. the selectivity, was probably influenced by the different possible environments of the site due to the presence of molybdenum, cobalt, oxygen, sulfur, potassium, and aluminum. With promoted MoS_2 a similar situation may be present except that in this case there is no cobalt or aluminum, and very little oxygen. The presence of sulfur and alkali near the anionic vacancies probably enhances chain growth and hence large selectivities to C_5+ products are obtained on alkali promoted MoS_2 catalysts.

3.4.4 Summary

- Molybdenum disulfide promoted with KOH was active for the FT synthesis.

- The selectivity to condensed products was high with relatively little CH_4 or CO_2 formation. This selectivity was high even at 400°C and $H_2/CO = 3$, conditions which normally favor methanation.

- The condensed products contained only a small amount of n-paraffins.

3.5 Tungsten-Based Catalysts

3.5.1 Catalyst Pre-treatment and Sulfiding

The catalysts used were commercial hydrotreating catalysts made by Harshaw Chemical Company. A 10% WO_3/Al_2O_3 catalyst, commercial name W-0801, was used after being impregnated with K_2CO_3 corresponding to 3.42 wt % K_2O. A 3% Ni-oxide + 10% WO_3/Al_2O_3 catalyst, commercial name W-0404, was used (a) without any alkali promoter, and (b) after being impregnated with K_2CO_3 so that the alkali content, calculated as K_2O, was 3.30 wt % of the total catalyst.

The reactors, after being loaded with the catalysts as shown in Table 3.33, were assembled on the unit and flushed and pressure tested with He. The catalysts were then dried overnight with flowing He at 200°C. Reactors 1, 2, and 3 were closed off and held under a He pressure of 500 kPa. Catalysts in reactors 5, 6, and 7 were treated in H_2, 720 V/V/h, at atmospheric pressure as follows: the temperature was increased in 50°C increments up to 450°C, and the catalysts were then reduced at 450°C for 23 h. At the end of this H_2 treatment the catalysts were flushed with He and reactors 5, 6, and 7 were closed off and kept under He at 500 kPa.

Catalysts in reactors 1, 2, and 3 were calcined in air, 480 V/V/h, at 400°C for 2 h. The temperature was reduced to 42°C, and the reactors were flushed with He. A flow of 10% H_2S in H_2, 600 V/V/h, was started; the temperature did not exceed 42°C. The temperature was kept at 42°C for 45 min, then raised to 150°C for 1 h and finally increased to 320°C. Sulfiding was continued with the 10% H_2S/H_2 mixture at 320°C for 14 h, after which the reactors were flushed with He. Catalysts in reactors 1, 2, and 3 will be called fully sulfided catalysts. The sulfiding procedure was recommended by Harshaw. All pre-treatment and sulfiding procedures were carried out at atmospheric pressure.

Table 3.33 summarizes the catalysts and the individual pre-treatment procedures.

Table 3.33

Summary of Catalysts in Run 7

Symbol	Reactor[1]	Catalyst[2]	Pre-treatment
WK-R	5	W-0801 + K_2O	Reduced in H_2
WK-S	1	W-0801 + K_2O	Calcined and fully sulfided
NW-R	6	W-0404	Reduced in H_2
NW-S	2	W-0404	Calcined and fully sulfided
NWK-R	7	W-0404 + K_2O	Reduced in H_2
NWK-S	3	W-0404 + K_2O	Calcined and fully sulfided

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[1] Reactor 4 contained MoS_2 promoted with KOH which was discussed in Section 3.4.

[2] 50 cm^3 of 60-120 mesh particles were used in each reactor. The weight of catalyst W-0801 + K_2O loaded into each reactor was 43.6 g, the weight of catalyst W-0404 loaded into each reactor was 46.9 g, and the weight of catalyst W-0404 + K_2O loaded into each reactor was 49.5 g.

At the end of run 7, the catalyst to be analyzed was removed from each reactor in equal sections in order to obtain a detailed longitudinal sulfur gradient (Table 3.34). Each section corresponded approximately to 5 cm of reactor length. In Table 3.34, 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 and so on.

Table 3.34

Longitudinal Sulfur Distribution in Catalyst Beds for Run 7

Catalyst	WK-S	NW-S	NWK-S
Section	Reactor 1 % S by wt	Reactor 2 % S by wt	Reactor 3 % S by wt
1	0.55	0.68	0.83
2	0.57	0.71	0.92
3	0.62	0.73	1.00
4	0.62	0.76	1.11
5	0.60	0.76	1.09
6	0.65	0.79	1.18
7	0.65	0.77	1.15
8	0.63	0.79	1.26
9	0.64	0.85	1.26
10	0.66	0.77	1.32
11	0.70	0.75	1.45
12	0.73	0.87	1.52
13	0.77	0.97	1.55
14	0.80	1.51	1.53
15	0.84	1.10	1.64
16	0.87	1.25	1.75
17	0.92	1.34	1.77
18	0.98	1.40	1.87

Two interesting points may be noted from Table 3.34. First, in all cases, there is more S at the exit than at the entrance of the reactor and is therefore unlike the S gradients measured on any of our other catalysts. There was probably a significant movement of S during run 7, and the S shifted from the catalyst near the entrance to the catalyst near the exit. It is also probable that some S was removed from the catalyst during the run. The second point is that under the same sulfiding conditions the amount of S on a catalyst varies according to the type of catalyst as follows:

NWK-S > NW-S > WK-S

The addition of nickel and alkali promoters to an alkalized W-based catalyst enhances the sulfur uptake by about a factor of 2.