FISCHER-TROPSCH SYNTHESIS ON CHARCOAL-SUPPORTED MOLYBDENUM: THE EFFECT OF PREPARATION CONDITIONS AND POTASSIUM PROMOTION ON ACTIVITY AND SELECTIVITY

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ABSTRACT

High dispersion and high activity charcoal-supported molybdenum catalysts were prepared using incipient wetness and equilibrium adsorption methods. Activities and selectivities of these catalysts were tested after reducing the catalysts at 773 K in flowing hydrogen. It was found that all the catalysts, particularly those prepared by the equilibrium adsorption method, showed high activities in Fischer-Tropsch synthesis of C_1 to C_3 hydrocarbons. Potassium promotion increased the selectivity towards C_2 and C_3 hydrocarbons while reducing moderately the activity. Without potassium promotion, C_2^+ selectivities of all the catalysts with metal loading of three weight percent or higher were about 50 ± 5% under differential reactor conditions. Promotion by potassium increased the C_2^+ selectivity to as much as 70%. It was found that there was a critical potassium loading at which point the activity decrease levelled off. The method of potassium addition to the catalyst also plays a major role in determining the final activity.

INTRODUCTION

Catalysts based on supported molybdenum compounds are extensively used in selective oxidation and hydrodesulfurization reactions [1,2], but due to their moderate activity they have not gained much popularity as synthesis gas conversion catalysts.

Schultz et al. [3] first investigated the catalytic properties of molybdenum group metals and concluded that only Mo had moderate activity. Unsupported Mo compounds including the sulfide, carbide, nitride and oxide were investigated by Leclercq et al. [4] and by Saito and Anderson [5]. These investigators found that the specific activity of these compounds (based on the number of active sites) were comparable to the best metallic catalysts. However, due to the low surface area and number of active sites per unit catalyst weight the overall activities were not very high. Despite their moderate activity, Mo based catalysts have good sulfur tolerance and are good water-gas shift catalysts. Thus they can be used with synthesis gas of low H_2/CO ratios without needing the expensive sulfur removal process required by the other metallic catalysts.

Much of the published fundamental research is about the properties and activity

of molybdena/alumina catalysts [6-8]. Molybdena/alumina systems exhibit strong chemical interaction between the support and molybdena, and it is not possible to obtain zero valent Mo on alumina supports [8] with low metal loadings. As a result, molybdena/alumina is a selective but low activity methanation catalyst [9,10]. By dehydroxylating the alumina and using molybdenum hexacarbonyl as the starting material, Brenner [11] has obtained catalysts that are orders of magnitude more active than the regular molybdena/alumina catalysts. However, these catalysts lose all of their extra activity rather rapidly when exposed to synthesis gas atmosphere.

Our primary objective in this research project was to prepare highly dispersed and active molybdenum-based Fischer-Tropsch (FT) synthesis catalysts. We have decided to use charcoal as the support because, compared to alumina, it is considered to be inert and previous work by Murchison [12,13] indicated that it was possible to obtain low valent Mo on carbon supports. Murchison's work also showed that Mo/carbon catalysts were fairly active and selective for low molecular weight hydrocarbon ($<C_6$) synthesis from CO and H_2. Bridgewater et al. [14] also studied charcoal-supported Mo catalysts for FT synthesis. There is, however, one major difference between the results of Murchison and Bridgewater. Murchison found that potassium could be used as a promoter to increase the C_2^+ selectivity of his catalysts without deactivating the catalyst significantly; Bridgewater et al. on the other hand, found that potassium is a very strong poison for their catalysts. In order to resolve this controversy we also did extensive experiments with promoted catalysts.

EXPERIMENTAL
Catalyst preparation

Both the incipient wetness method (IW) and the equilibrium adsorption (EA) techniques [8,15] were employed to prepare the catalysts. For IW catalysts, the following general procedure was used: solutions of appropriate concentrations were prepared from ammonium heptamolybdate, AHM (Fisher Scientific Co.) or molybdenum oxalate (supplied by Climax Molybdenum Co.). pH's of the solutions were adjusted using nitric acid or ammonium hydroxide. A volume of solution equal to the pore volume of the support was added to the support contained in a beaker while stirring the mixture to insure uniformity. The sample was allowed to stand for an hour at room temperature and then air dried for 24 hours at 373 K for AHM and 353 K for oxalate catalysts. Equilibrium adsorption (EA) catalysts were prepared by slurrying the support for 24 hours in a solution containing 1% Mo by weight, longer slurrying did not change the loading. The volume of the solution was 250 cc and the weight of the support was only 5 grams. This insured that there were no significant changes in the solution due to adsorption by the support. After slurrying, the catalysts were filtered off and air dried at 373 K for 24 hours. Mo load-

ing of the equilibrium adsorption catalysts were determined by neutron activation analysis. Mo loading of the incipient wetness catalysts were both determined from the amount of Mo used in the filling solution and neutron activation analysis. The results obtained from both methods agreed within the experimental error.

In order to determine whether the support had any significant effect on the activity and selectivity, we used two different charcoals as support. Besides, a low surface area titania (Degussa P25) was used to check the activity and select- ivity of the same catalyst on a low surface area, non-porous support. The first charcoal support was obtained from Fisher Scientific (Darco G-60) and had a BET surface area of 800 $m^2 g^{-1}$ and a pore volume of 1 $cm^3 g^{-1}$, particle size of 100- 325 mesh. Unfortunately, we did not have any information regarding the pore size distribution or the exact chemical composition of this support. The second char- coal support was a sample from Calgon, CPG activated carbon. This support had a BET surface area of 1100 $m^2 g^{-1}$, particle size of 12-40 mesh, pore volume of 0.9 $cm^3 g^{-1}$, and a bimodal pore size distribution. According to the manufacturer, at least 50% of the pore volume of this support was due to pores with diameters larger than 20 Å. This support contained 0.5% Na, 0.02% K, 0.15% Fe and 0.002% Cu by weight according to the manufacturer. The BET surface area of the titania support was found to be 50 $m^2 g^{-1}$, the same as given by the manufacturer. Potassium load- ing was achieved by incipient wetness with a solution of potassium carbonate of the appropriate concentration and then air drying. For IW catalysts, potassium addition was done before the Mo loading; for the EA catalysts, potassium was loaded after the Mo loading.

Catalyst pretreatment and testing

After air drying, the catalysts were loaded into a stainless steel reactor for reduction treatment and determination of their activities and selectivities. The reactor itself was a 75 mm long, 25 mm O.D. and 2.5 mm I.D. tube. Typically, a sample of 0.15 to 0.30 g of dried catalyst was loaded into this differential react- or. Temperature of the gaseous mixture inside the reactor was monitored and controlled within ± 1 K by an Omega temperature controller. Flow rates of the reactant gases were controlled to ± 1% of the desired flow rate by a Matheson mass flow control system. Flow rates that gave space velocities in the range of 6000 h^{-1} to 12000 h^{-1}, depending on the catalyst, were used to produce the reaction conversion in the differential reactor range (conversion < 10%). Product analysis was performed using a Hewlett Packard 5710A gas chromatograph equipped with dual thermal conductivity detectors. Separation of the products was achieved with a 3 m long, 3 mm diameter Chromosorb 102 column and linear temperature programming for the oven from 20°C to 150°C. Peak areas were integrated by a Hewlett Packard 3390A programmable integrator. Water, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{10}, C_5H_{12} and C_6H_{14} could all be clearly separated and quantitatively measured. The

response factors of the GC detector used for these components were experimentally determined using the appropriate calibration gases. In particular, the Matheson 77-284 calibration gas cylinder was used for C_1 to C_6 n-paraffins. Except for water, all the response factors determined were in good agreement with that report- ed by Dietz [16]. A mass balance program based on the conservation of carbon and oxygen elements was installed in a HP 9835A minicomputer to check if all the carbon and oxygen in the feed stream have been detected and accurately accounted for in the exit stream. The mass balance on carbon could be closed within ± 4%. But the error from the mass balance on oxygen was found to be as large as 12%. This was due to the inaccuracy in determining water amount in the products since water peaks often tailed badly. Therefore, the mass balance in oxygen was not used in this study. Also, 2% of N_2 gas was introduced in the feed to serve as an internal standard for mass balance. However, the peak of N_2 was found to overlap with the peak of CO and the quantization of N_2 amount could not be obtained with errors less than ± 15%. Therefore, all the data reported in this study were based on the mass balance of carbon element only. Considering the accuracy of our flow controlling system, this method is reliable. After some preliminary experimentation with increasing reduction temperatures from 623 K to 823 K and times from 2 hours to 12 hours with flowing hydrogen it was found that the maximum in activity was reach- ed at a reduction temperature of 723 K and a reduction period of five hours. Increasing the reduction temperature to 773 K did not increase the activity further but caused a moderate increase in the desired C_2^+ selectivity. Increasing the reduction temperature above 773 K resulted in a slight decrease in activity and a rather large decrease in C_2^+ selectivity. Increasing the reduction period from 5 hours to 8 hours did little to change the activity or C_2^+ selectivity. But when the catalyst reduction period was further increased from 8 hours to 12 hours, its C_2^+ selectivity increased slightly but its activity dropped significantly. There- fore, all the catalysts used in this study were reduced at 773 K for five hours. For the comparison of activities and selectivities among the catalysts used, reaction conditions of 573 K, 0.12 Mpa, and feed H_2/CO ratio of 3 were used. Reactions in the temperature range of 543 to 663 K were also performed to deter- mine the apparent activation energy and the effect of temperature on C_2^+ select- ivities. Feed H_2/CO ratios from 0.5 to 10 were used in the determination of the apparent rate expression for the FT synthesis at 573 K and 0.12 MPa.

Wide Angle X-ray Spectroscopy (WAXS) technique was also used to characterize the catalysts used. Samples were allowed to cool down to room temperature from either reduction temperature or reaction temperature in flowing hydrogen. Then the samples were taken out from the reactor (therefore, exposed to air) and taken to a Philips X-ray diffractometer using CuKα irradiation for WAXS analysis. Powder diffraction pattern of pure Mo_2C and MoO_2 were also taken to serve as the reference for determining the relative amounts of Mo_2C and MoO_2 in the samples used.

TABLE 1

Properties of unpromoted Mo catalysts.

Catalyst	Precursor	Type of support	% Mo loading[a]	Initial pH	Final pH
IW-1	AHM	G-60	3	5.2	-
IW-2	AHM	G-60	6	5.2	-
IW-3	AHM	G-60	6	2.0	-
IW-4	AHM	G-60	12	5.2	-
IW-5	AHM	CPG	6	5.2	-
IW-6	AHM	CPG	12	5.2	-
IW-7	AHM	CPG	1	2.0	-
IW-8	AHM	CPG	1	9.0	-
IW-9	AHM	TiO_2	9	5.2	-
IW-10	MoOx	G-60	6	5.2	-
EA-1	AHM	CPG	16	1.2	1.4
EA-2	AHM	CPG	18	2.0	2.1
EA-3	AHM	CPG	11	5.2	5.5
EA-4	AHM	CPG	1	9.0	9.4
EA-5	AHM	G-60	16	2.0	2.3
EA-6	MoOx	CPG	12	1.6	1.7
EA-7	MoOx	CPG	8	4.0	5.1

[a]calculated as wt% of elemental Mo.

Crystallite sizes of the samples were determined from line-broadening of the X-ray peaks. To confirm the detected particle sizes from WAXS, transmission electron microscopy (TEM) technique was conducted using a Philip EM-400 high resolution transmission electron microscope operated at 100 kV.

RESULTS AND DISCUSSION

Table 1 gives the molybdenum loading of all the unpromoted catalysts used in this study.The most surprising point about Table 1 is the high loadings of the EA catalysts obtained from a 1 wt% solution just by varying the pH. In going from pH of 9 (at which pH there is no enhancement of adsorption) to pH of 2, the loading increases by a factor of 18! Strongly pH dependent equilibrium adsorption has been observed for supports with surface hydroxyls, such as alumina, titania, and magnesia [8,15]. While it is normal to expect pH dependent anion adsorption onto supports with surface hydroxyls, it is rather surprising to find that charcoal adsorbs more than twice the amount that alumina does at pH 2 (18% Mo as compared to 9%). At this point we are not sure whether the adsorption is only due to surface

RATE (Mole CO/gm-Moly/sec) *10E+6   RELATIVE SELECTIVITY C2+/HC (%)
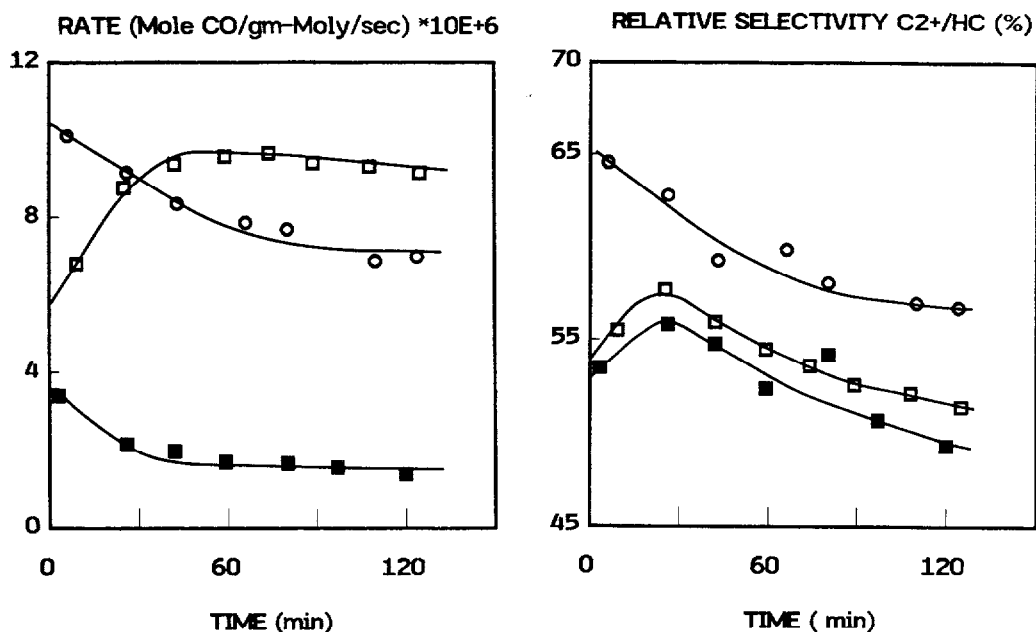
FIGURES 1 and 2   Activity and selectivity (C_2^+/HC) as a function of time during the first two hours of reaction for three representative catalysts. Reaction conditions used: 573 K, 0.12 MPa, H_2/CO = 3. Symbols:◯, IW-5,▢, EA-2,■, IW-9 catalysts. In Figure 1, the initial period which the EA catalyst gains activity is attributed to carburization of the surface. In Figure 2, the selectivity pattern of Mo/TiO_2 (IW-9) catalyst is the same as the EA AHM catalysts.

hydroxyls or not. Hall [15] explained the increased adsorption on alumina and titania as being purely a function of the solution pH. In our experiments with AHM and Mo-oxalate solutions we found [17] that the amount of Mo adsorbed depends on the type of the anion present in solution as well as the solution pH. This can be seen clearly from the differences in Mo loadings between the AHM and oxalate based catalysts given in Table 1. The loadings of the oxalate catalysts are lower than the corresponding AHM loadings.

BET surface area measurements were made on several selected catalysts. It was found that the total surface area of catalyst decreased with metal loading irrespective of the method of loading. For the IW catalysts the reduction in the BET area ranged from 3.6% to 4% for each weight percent of Mo loading. The EA catalyst exhibited a somewhat less decrease in BET areas (2.5% to 3.0% for each weight percent of Mo loading). Since the volume of Mo and its oxides present are not enough to cause the reduction just by filling the micro-pores of the supports, the large decrease in BET area can be explained by a pore mouth or throat blocking mechanism for the very small pores. The decrease in surface area was comparable
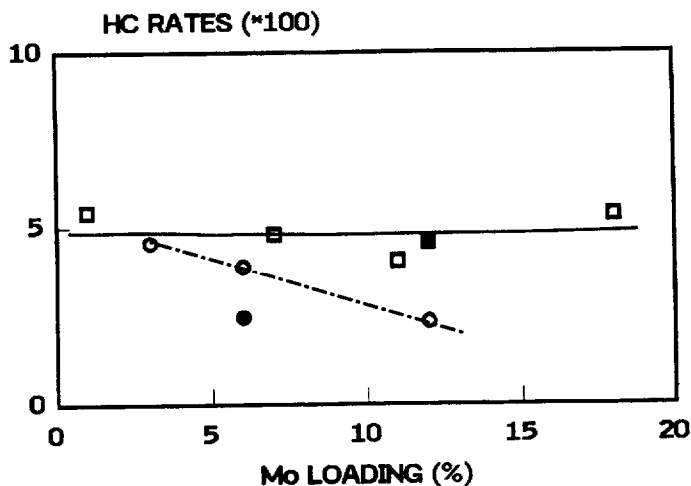
HC RATES (*100)

FIGURE 3   Reaction rate (mole CO reacted to HC/mole Mo atom-min) as a function of Mo loading (%). The rate decreases with increasing loading for IW catalysts while there is no such trend for EA catalysts. Reaction conditions as that given in Figure 1. Symbols:○, IW-1,2,4;●, IW-10;□, EA-2,3,4;■, EA-6 catalysts.

for AHM and Mo-oxalate based catalysts. In order to get an idea of the particle size and the composition of our catalysts, wide angle X-ray spectroscopy (WAXS) of a representative sample of each group was measured using the procedures described in the experimental section. From these results we deduced that the IW catalysts contained MoO_2. The crystallite sizes determined from line-broadening using Scherrer's equation were 250 ± 50 Å. The EA catalysts spectra consisted of very broad peaks, the presence of which were barely detectable above the background. MoO_2 and Mo_2C were detectable with estimated crystallite sizes of 110 ± 50 Å and 140 ± 50 Å respectively. The relative amount of them was found to be 88 ± 5% MoO_2 and 12 ± 5% Mo_2C. The particle sizes determined by our TEM measurements gave a range of 40 to 250 Å for IW catalysts and 40 to 150 Å for EA catalysts, also in good agreement with our WAXS data. We should point out that the WAXS measurements are weighted towards the large crystallites since WAXS does not see crystallites below 50 Å. Also in the electron microscope crystallites smaller than 40 Å were not easily detectable due to contrast problems. Thus only the upper end of the crystallite sizes is reliable.

Activity and selectivity

When first brought on stream the activity of the catalysts were low. The IW catalysts reached a maximum in activity within the first few minutes of being on stream. The EA catalysts reached their peak activity after being on stream for an

TABLE 2

Comparison of the activity of some Mo catalysts used in this study with literature values

Catalyst	Reaction rates[a] at 623 K
IW-10	0.122
IW-9	0.035
IW-2	0.173
EA-6	0.202
EA-2	0.238
Harshaw Ni-0104	2.901
Mo_2C/C[b]	0.019
MoO_2/C[b]	0.017
Mo_2C[c]	0.086
Mo_2C[d]	0.018
MoO_2[d]	0.006
Mo	0.006

[a]Reaction rates are in the units of (mole of CO reacted to HC/mole of Mo atom-min)
[b]from reference [14]
[c]from reference [19]
[d]from reference [5].

hour or longer. Figure 1 shows this difference between the two types of catalysts, the reaction conditions were fixed at 573 K, 0.12 MPa, and H_2 to CO feed ratio of 3. After reaching the peak, activity for both catalysts started decreasing slowly with time and the decrease levelled off at about 60 to 80% of the maximum activity in ten hours, depending on the catalyst. Instead of using the initial or maximum activity which is hard to define, the activity value at time equal to two hours was used in this study. The initial period during which the catalyst gains activity has been observed before [5,14] and is attributed to carburization of the surface. Since the EA catalysts were found to exhibit higher dispersion, the carburization of their surface took longer. The non-porous titania-supported catalyst exhibits exactly the same activation and deactivation behavior as the IW catalyst. Figure 2 shows the change in selectivity as a function of time for the same catalyst. It is interesting to note that the titania supported catalyst behaves like the EA catalyst in its selectivity, even though it was prepared by the incipient wetness method.

Figure 3 shows the reaction rates of the IW and EA catalysts prepared from AHM and Mo-oxalate as a function of Mo loading. Our rates are based on the moles of CO

feed and have the unit of moles of CO reacted to hydrocarbons/moles of total Mo atom min. Due to the great affinity of the charcoal support for CO [14,18], chemisorption surface areas were not measured. We also feel that overall this is a much more relevant quantity than the turnover number which is based on the number of active sites only. Besides, the activity of Mo/charcoal catalysts has not been reported in true turnover number in literature. This rate decreases with increasing loading for the IW catalysts. There is no such trend for the EA catalysts. The only data point we have for an oxalate-based IW catalyst shows a 30% lower activity. On the other hand, the EA Mo-oxalate catalyst has the same activity as the EA AHM catalysts. For the IW catalysts, we also made a study of the effect of the pH values of the starting solution and detected no significant differences in activity and selectivity as long as the support was the same.

To make a valid comparison of activity we have listed the rates for a representative number of our own catalysts along with values obtained by other investigators using molybdenum based catalysts in Table 2. Since the reaction temperature used in most previous studies was 623 K, the values given in this table are at 623 K and not at 573 K, the reaction temperature we used. In order to convert our activity values to that of 623 K, we carried out the same reaction on each of the two kinds of catalyst (IW-2,EA-2) over the temperature range of 543 K to 663 K and determined the apparent activation energy. We then converted our activity data at 573 K to 623 K based on our activation energy value. It can be seen that, with the exception of the titania supported IW catalyst (IW-9), all of our catalysts are much more active than other Mo based catalysts. The activities of our best catalysts approach 8% of the activity of the commercial nickel hydrogenation catalyst. One advantage of our catalyst is the high C_2^+ selectivity, the commercial nickel catalyst produced 96% methane as compared to 47% methane for our catalyst. Besides, since coking and wax formation is not a serious problem for carbon supported Mo catalysts, the difference in activity can easily be gained by operating at only about 75 K higher than the Ni catalyst. Slightly higher temperature is actually a bonus in terms of controlling a highly exothermic reaction like FT synthesis. The most relevant study to compare our results with is that of Murchison's [11,12], but he does not give any absolute activities in his papers. Besides, exact comparison cannot be made because the reaction conditions used in his study are different from that of this study (He had higher pressure, higher conversion data as compared to ours at low pressure, and low conversions). As can be seen from Figure 1, the peak in activity was reached long after the start-up. If the active species of our catalysts are the molybdenum carbides then it is possible that we may have formed either higher dispersion and/or different types of surface carbides compared to the previous investigations.

Table 3 shows the selectivities of all of our catalysts to methane, ethane and propane, the only hydrocarbons produced in detectable quantities. Trace of butane

TABLE 3

Comparison of the activity and selectivity of unpromoted Mo catalysts used in this study[a]. Nickel catalyst is included for comparison.

Catalyst	Rates[b] * (100)	mole% C_1[c]	C_2/C_1[d]	C_3/C_1[d]	HC/CO_2
IW-1	4.56	47.1	0.95	0.17	1.27
IW-2	3.89	44.0	0.94	0.34	1.28
IW-3	3.98	42.9	1.04	0.29	1.13
IW-4	2.32	47.9	0.93	0.16	1.09
IW-5	2.31	48.1	1.01	0.06	1.16
IW-6	2.47	44.3	1.03	0.23	1.11
IW-7	1.86	60.8	0.64	0.00	2.69
IW-8	2.08	58.1	0.72	0.00	2.07
IW-9	0.79	49.1	0.98	0.05	1.03
IW-10	2.73	45.6	1.00	0.19	1.24
EA-1	4.24	44.5	0.89	0.35	1.13
EA-2	5.35	47.3	0.78	0.33	1.14
EA-3	4.05	47.0	0.85	0.28	1.15
EA-4	5.44	70.5	0.39	0.03	0.87
EA-5	4.14	46.5	0.89	0.26	1.10
EA-6	4.54	48.8	0.75	0.30	1.05
EA-7	2.30	42.9	1.08	0.25	1.12
Ni-0104	65.10	96.2	0.03	0.005	13.30

[a] reaction conditions: 573 K, 0.12 MPa, H_2/CO = 3.
[b] rates units as given in Table 2.
[c] selectivity is defined as $nCn/\Sigma nCn$, or mole% of total carbon converted to hydrocarbons.
[d] C_2/C_1 and C_3/C_1 are based on moles of carbon in each species.

was also detected for some of the higher activity catalysts (no more than 5% of propane or 0.5% of total hydrocarbons). All of the selectivities reported here are for reactions under differential reactor conditions, i.e. around 10% or less conversion. Also shown in the table are the ratios of the total hydrocarbons produced to the carbon dioxide produced. With the exception of low Mo loading catalysts IW-7, IW-8 and EA-4, there are no striking differences between the remaining catalysts. These low Mo loading catalysts exhibit very high methane selectivities. There is, however, a slight but significant difference between the EA catalysts and the IW catalysts. The EA catalysts show lower total HC/CO_2 selectivity. There is also a small but consistent difference between the C_2/C_1

TABLE 4

Comparison of the selectivity of some catalysts used in this study[a] with literature and Schultz-Flory distribution prediction

Catalyst	$\%C_1$ [c]	C_2/C_1 [c]	C_3/C_1 [c]	HC/CO_2	C_2/C_1 [d]	C_3/C_1 [d]
IW-10	45.6	1.00	0.19	1.24	0.65	0.32
IW-9	49.1	0.98	0.05	1.03	0.60	0.27
IW-2	44.0	0.94	0.34	1.28	0.67	0.34
EA-6	48.8	0.75	0.30	1.05	0.60	0.27
EA-2	47.3	0.78	0.33	1.14	0.62	0.29
Ni-0104	96.2	0.03	0.005	13.30	0.04	0.00
Mo_2C/C [b] [e]	59.5	0.41	0.00	0.93	0.46	0.16
MoO_2/C [b] [e]	62.7	0.32	0.00	0.99	0.42	0.13
Mo_2C [f]	52.3	0.79	0.12	N/A	0.55	0.23
Mo_2C [a] [g]	53.9	0.53	0.16	N/A	0.53	0.21
MoO_2 [a] [g]	64.7	0.20	0.05	N/A	0.39	0.12

[a] reaction conditions: 573 K, 0.12 MPa, H_2/CO = 3
[b] selectivity corrected to 573 K, assuming the changes in selectivity with temperature is of the same fashion as our catalysts
[c] as defined in Table 3
[d] Schultz-Flory prediction, from reference [13]
[e] from reference [14]
[f] from reference [20]
[g] from reference [5]

ratios of EA and IW catalysts. The IW catalysts have higher C_2/C_1 ratios. In contrast, the EA catalysts have higher average C_3/C_1 ratios.

Strong conversion dependence of selectivity in FT synthesis makes quantitative comparisons difficult. However, in order to get at least a qualitative idea, we have listed the selectivities of some of our catalysts along with literature values in Table 4. It is clearly seen from the HC/CO_2 ratio that there is good agreement between the various investigations and that this ratio is almost a constant, independent of the catalyst. This is probably due to a strong coupling between the synthesis reaction (1) and the water gas shift reaction (2):

$$nCO + (2n+1)H_2 = C_nH_{2n+2} + nH_2O \qquad n=1,2,3... \qquad (1)$$
$$CO + H_2O = CO_2 + H_2 \qquad (2)$$
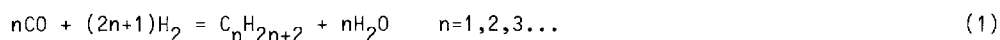
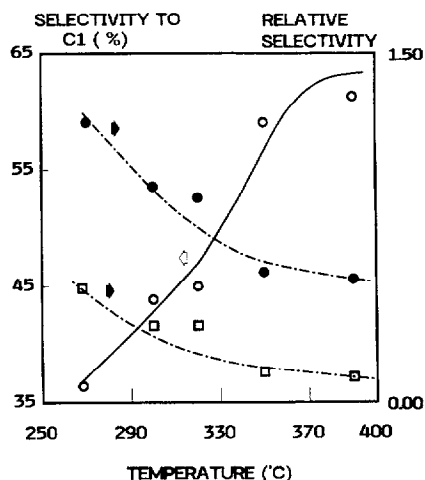Since all the Mo compounds are good shift catalysts, at 573 K the conversion in

FIGURE 4   Selectivity as a function of temperature of EA-2 catalyst at 0.12 MPa and H_2/CO = 3. As temperature increases, selectivity to C_1 increases, and relative selectivity of C_2/C_1 and C_3/C_1 decreases steadily. Symbols:$\bigcirc$, selectivity to C_1; $\bullet$, relative selectivity C_2/C_1; $\square$, relative selectivity C_3/C_1.

reaction (2) is close to its equilibrium value [5]. The C_2/C_1 ratios of our cata-lysts are close to 1.0. In comparison, C_2/C_1 ratios of the other catalysts reported in literature range from 0.2 to 0.53. Only Kojima et al's [19] bulk carbide has a high value. Since our Mo loadings are comparable to the others', the difference can only be due to the nature of the active sites. We have also listed the Schultz-Flory distribution prediction based on the methane fraction of the total hydro-carbons produced. It is clearly seen in the table that our C_2/C_1 ratio is signifi-cantly higher than the prediction. At this moment we are not sure about the exact reasons for this discrepancy. One possibility is that because the Schultz-Flory prediction is based on the assumption that a wide distribution of hydrocarbons (say up to C_{20}) is produced, our results may not be directly comparable to it since our catalysts produced only C_1 to C_3. Another possibility is that some of the methane is formed on sites which do not take part in the synthesis of higher hydrocarbons.

  Like the C_2/C_1 ratios our C_3/C_1 ratios are also high compared to the values reported in the literature. The prediction of the Schultz-Flory distribution is comparable to the observed values.

  In order to test the effects of temperature and pressure on selectivity and activity we tested one IW and one EA catalyst at several temperatures and pressures. From the hydrocarbon activity measured at low conversions we obtained an activation energy of 21.2 kcal $mole^{-1}$ for IW and 20.8 kcal $mole^{-1}$ for EA catalyst respectively. These values are in good agreement with Murchison's value of 22.8 kcal $mole^{-1}$ [12]. For IW catalyst, the rate was found dependent on approximately the 1.1 power of
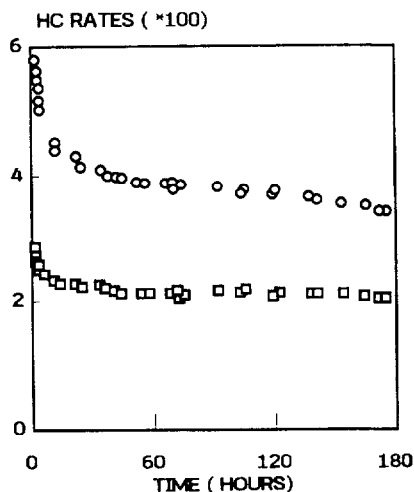
HC RATES (*100)

FIGURE 5 Long term performance (up to 7 days) of a representative EA catalyst (EA-2) under our standard reaction conditions: 573 K, 0.12 MPa, H_2/co = 3. Rate unit as that given in Figure 3. Symbols:$\bigcirc$, HC rate;$\square$, CH_4 rate.

the total pressure, while for EA catalyst the dependence was found to be around 1.4 power. The partial pressure dependences were found to be 0.7 on H_2 and 0.4 on CO for IW catalyst, and 0.9 on H_2 and 0.5 on CO for EA catalyst. None of these partial pressure dependences agree with that reported by Murchison et al. [12] as the partial dependence was 0.5 for H_2 and 1.0 for CO in his report. This was probably due to the different reaction mechanisms involved in our differential reactor and his Berty High Recycle Reactor operated at higher pressures and higher conversions. As for the selectivity, we found that higher temperature shifted the selectivity towards more methane, as expected. Increased pressure does not have a significant effect on selectivity, but this may be due to the narrow range of pressure used. We also note that as the conversion increases (within in the differential reactor range) the C_2^+ selectivity does not change. Figure 4 shows the changes in selectivities as a function of temperature. As expected, the methane selectivity increases at the expense of C_2^+ selectivity.   We also observed that the HC/CO_2 activity ratio stayed constant with increasing temperature. In order to have an idea about the relation between our activity values (at time equal to two hours) and steady state activity, long term performance of both EA and IW catalysts were measured for 7 days. The deactivation behavior of one representative catalyst (EA-2) is shown in Figure 5. Since we have found that the deactivation of all catalysts is similar, the use of our activity values is appropriate.

Effect of charcoal support

In order to find out whether the type of support used was as crucial as

TABLE 5
Properties of promoted Mo catalysts

Catalyst	Precursor	Type of support	% Mo[a] loading	% Potassium[b] loading	Initial pH
IW-K-1	AHM	G-60	6	0.00	5.2
IW-K-2	AHM	G-60	6	0.16	5.2
IW-K-3	AHM	G-60	6	0.64	5.2
IW-K-4	AHM	G-60	6	2.00	5.2
EA-K-1	AHM	CPG	18	0.00	2.0
EA-K-2	AHM	CPG	18	0.20	2.0
EA-K-3	AHM	CPG	18	0.60	2.0
EA-K-4	AHM	CPG	18	2.00	2.0

[a] calculated as wt% of elemental Mo
[b] calculated as wt% of elemental K.

Bridgewater et al. [14] claimed we prepared two IW and two EA catalysts with two charcoal supports under exactly identical conditions. Upon testing their activity we found out that the 6 wt% G-60 charcoal supported IW catalyst had approximately 1.6 times the activity of the CPG charcoal supported IW catalyst. In sharp contrast, the pH 2, CPG supported EA catalyst had approximately 1.4 times the activity of the G-60 supported one. From these results we conclude that there may be a mild support effect, but the direction of the effect depends on the method of preparation used.

Potassium promotion

Since it is well known that promotion with alkali metals increases the average molecular weight of products in FT synthesis, we promoted some of our catalysts with potassium to improve the C_2^+ selectivity. Table 5 lists the properties of the promoted Mo catalysts prepared in this study. Figure 6 shows the changes in selectivity and activity for a 6% IW and a 18% EA catalyst.

Potassium (in the form of carbonate) was added to the IW catalyst before the AHM loading and to the EA catalyst after the AHM loading. We see that the major decrease in activity occurs at 0.16 wt% of K for the IW catalyst and that there is no change in activity all the way from 0.16 to 2.0 wt% of K. In comparison, the EA catayst activity continues decreasing with K loading until at about 1 wt% K loading. The decrease in activity of the EA catayst is almost tenfold as compared to a decrease of only threefold for the IW catalyst. The C_2^+ to C_1 ratio doubles for the IW catalyst and increases by only 50% for the EA catalyst. The rate and relative selectivities of methane, ethane, ethylene and propane are shown in Table 6. The effect of potassium in activity shown in Figure 6 is very similar to the
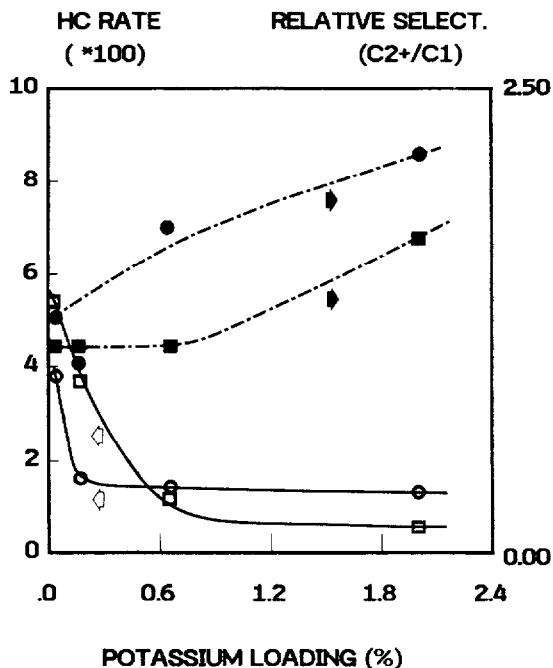
FIGURE 6 Reaction rate (mole of CO reacted to HC/mole of Mo atom-min) and relative selectivity (C_2^+/C_1) as a function of potassium loading. Symbols: ○,●, for IW catalysts and □,■, for EA catalysts. Open symbols are for the rate, and darkened symbols are for relative selectivity.

effect observed on a single nickel crystal [20].

Apart from improving the C_2^+ selectivity, addition of potassium also increases the relative activity towards CO_2 production. The HC/CO_2 ratio of the promoted catalysts are about 30% lower than that of the unpromoted catalysts. This might be be due to the shift reaction not being affected as much by the potassium addition as the FT synthesis reaction.

In comparing the activities of our promoted and unpromoted catalysts, we find that there is certainly a decrease in activity due to potassium addition, but it is a moderate decrease, nowhere near the 200 fold decreases demonstrated by Bridgewater et al's [14] catalysts. Our findings are in agreement with those of Murchison's [12]. We think the larger decrease in the activity of the EA catalyst is due to the fact that potassium carbonate had to be added to this catalyst after Mo loading.

Figure 6 shows that there may be a critical K/Mo ratio beyond which the decrease in activity becomes negligible but the C_2^+ selectivity continues increasing. For the IW catalyst the levelling off point of K/Mo weight ratio is 0.026 and for the

TABLE 6

Comparison of the activity and selectivity of promoted Mo catalysts[a]

Catalysts	Rate *100	$\%C_1$	$C_2H_4/C1$	C_2H_6/C_1	C_2^+/C_1 [b]	HC/CO_2
IW-K-1	3.89	44.0	0.00	0.94	1.28	1.28
IW-K-2	1.57	49.9	0.31	0.69	1.00	0.82
IW-K-3	1.28	36.3	0.99	0.51	1.76	0.82
IW-K-4	1.28	31.5	1.53	0.27	2.17	0.85
EA-K-1	5.35	47.3	0.00	0.78	1.11	1.14
EA-K-2	3.65	47.7	0.01	0.79	1.09	1.09
EA-K-3	1.22	47.6	0.02	0.80	1.10	1.14
EA-K-4	0.55	36.7	0.97	0.69	1.72	0.79

[a] reaction conditions: 573 K, 0.12 MPa, $H_2/CO = 3$

[b] $\%C_1$ as defined in Table 3, definitions for C_2H_4/C_1 and C_2H_6/C_1 are similar to C_2/C_1 in Table 3, except that C_2 is now composed of C_2H_4 and C_2H_6. C_2^+ stands for the sum of C_2H_4, C_2H_6 and C_3H_8.

EA catalyst this ratio is approximately 0.050. Since the crystallite sizes of the EA catalysts are about half that of the IW catalysts we would expect a higher potassium loading before the surface electronic properties are affected to a similar degree.

CONCLUSION

This study demonstrates that, for the synthesis of C_1-C_3 hydrocarbons from CO and H_2, charcoal-supported molybdenum is a good catalyst. We have demonstrated that, without resorting to elaborate preparation methods, it is possible to prepare catalysts with higher activities than that of previously reported. We have also shown that equilibrium adsorption of AHM onto charcoal produces catalysts which have specific rates independent of Mo loading. These catalysts are also twice as active as the catalysts prepared by the incipient wetness method.

When used as a promoter in significant amounts, potassium increases the olefin and C_2^+ selectivities, and moderately decreases the activity of our catalysts. The decrease in activity levels off, whereas the selectivity continues increasing with potassium loading.

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