Chapter 3

SCREENING OF ALKALI-PROMOTED VAPOR-PHASE-SYNTHESIZED MOLYBDENUM SULFIDE CATALYSTS FOR THE PRODUCTION OF ALCOHOLS FROM SYNTHESIS GAS

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ABSTRACT

A series of molybdenum sulfide catalysts has been prepared using vapor-phase decomposition of molybdenum hexacarbonyl in an atmosphere of hydrogen sulfide. The effect of the decomposition conditions on the properties of the molybdenum sulfides formed has been studied over a temperature range of 300-900°C. These materials, when promoted with alkali, have been found to have a high activity for the production of alcohols from synthesis gas. The effects of the catalyst preparation temperature (*i.e.*, decomposition temperature) and reaction conditions (temperature, flow rate) have been studied, as well as the effect of the type and concentration of the alkali promoter. In all cases, the alcohols formed are primarily straight-chain, terminal -OH compounds. The variations in preparation procedure have only small effects on the conversion and the selectivity to higher alcohols. Increasing the reactant flow rate increases the selectivity to methanol at the expense of the hydrocarbons and the higher-molecular-weight alcohols. Increasing the reaction temperature changes the selectivity towards higher alcohols but also changes the selectivity towards hydrocarbons. A maximum in selectivity to higher alcohols with the reaction temperature is observed for all catalysts tested.

INTRODUCTION

Alcohols as well as other oxygenates derived from alcohols are viewed as desirable gasoline additives both to improve octane and to reduce engine emissions. Alcohols were certainly present in the liquid product of the original BASF-patented process (BASF, 1913) whereby CO was hydrogenated at high pressures and temperatures over an iron-based catalyst. However, current processes for making alcohols (other than methanol) from synthesis gas, a mixture of carbon monoxide and hydrogen, are limited by the sulfur stability and the selectivity of present-day catalysts.

Catalysts used for the production of higher alcohols from synthesis gas have been extensively reviewed by Klier *et al.* (1988a). Ponec (1992) recently speculated on the active centers of many of these catalysts. The catalysts can be divided into four categories. The first of these is a soluble Ru complex used as a homogenous catalyst. The second can loosely be described as modified methanol catalysts. This type of catalyst may operate at high pressure (*i.e.*, greater than 100 atm) or lower pressures, corresponding to the individual progenitor methanol-synthesis catalyst. Examples include alkali-doped ZnO/chromia catalysts and CuO-based catalysts respectively . The third category of higher-alcohol synthesis (HAS) catalysts comprises mixed-metal catalysts, *e.g.*, Rh and Fe on a support. The final category is chalcogenide-based, typically alkali-promoted MoS_2. This category of higher-alcohol synthesis catalyst is the focus of the present work.

Molybdenum sulfide catalysts promoted by alkali-metal compounds were discovered to be active for higher alcohol synthesis by research groups at Dow (see, *e.g.*, Murchison *et al.*, 1988) and Union Carbide (*e.g.*, Kinkade, 1984). Academic research groups such as those led by Klier (see, *e.g.*, Santiesteban *et al.*, 1988) and Somorjai (*e.g.*, Youchang *et al.*, 1986) have also studied molybdenum sulfide catalysts. Recently, the role of the promoter has been discussed by Lee *et al.* (1994). These catalysts are characterized by water-gas-shift capability and a very high tolerance for sulfur -- in fact, a pretreatment with H_2S is generally required.

The types of alcohols produced depend strongly upon the type of catalyst used. Typically, the MoS_2-based catalysts produce mainly linear alcohols, while certain lower-pressure modified methanol-synthesis catalysts (such as the K/CuO/Zn/Cr material used in the Lurgi process) produce mainly branched alcohols. The higher-pressure modified methanol-synthesis catalysts typically produce branched alcohols and linear alcohols. The temptation is therefore to assume two different mechanisms and two different types of reaction sites. This is analogous to the situation in the formation of hydrocarbons from synthesis gas by the Fischer-Tropsch process, where Lox and Froment (1993) hypothesized two different types of sites.

It is reasonable to expect that the nature of the MoS_2-based catalyst is governed by the morphology of the molybdenum sulfide, and that would depend upon the mode of preparation of the material. Molybdenum disulfide, MoS_2, has been prepared by thermolysis of MoS_3 (Eggersen and Roberts, 1959; Klier *et al.*, 1988) and of $(NH_4)_2MoS_4$ (Eggersen and Roberts, 1959; Wildervanck and Jellinek, 1964), by CVD (Suhr *et al.*, 1990), laser pyrolysis (Oyama *et al.*, 1989, 1994), and liquid- or vapor-phase decomposition (Chatzitheodorou *et al.*, 1988; Rice *et al.*,1992). The size of the particles, as well as their crystallographic phase and their chemical composition, can be altered by varying the decomposition variables. In the present work, we use a continuous-flow vapor-phase technique where molybdenum hexacarbonyl, $Mo(CO)_6$, is decomposed in hydrogen sulfide to produce molybdenum sulfides of varying characteristics. We then use the sulfides formed, with and without promoters, as catalysts for HAS from synthesis gas.

Below, we first describe the apparatus for the formation of the sulfides and the catalytic reactor system. The characterization of the sulfides, in terms of surface area, amount of sulfur, x-ray diffraction, and product yield is briefly provided. The results of the catalytic screening runs are then presented, along with specific experiments focussing on the alkali metals added as promoters.

EXPERIMENTAL

Sulfide Synthesis Apparatus. This is shown in Figure 1. Separate reservoirs are available in parallel for molybdenum hexacarbonyl and iron pentacarbonyl, so either single- or mixed-metal sulfides or carbides can be prepared. Here we are concerned only with the pure molybdenum sulfides. The inert gas, typically argon, is purified through molecular sieve and copper catalyst sections before being mixed with reactant H_2S. Flow rates of all gases are controlled by Matheson rotameters which were calibrated in-house. A Lindberg split furnace, controlled by a Eurotherm 818 programmable controller, is used for the thermolysis. The main tube through the furnace is fabricated from 0.9m (3 ft) of 25-mm quartz tubing. At the furnace entrance, a water-jacketed injection tube reduces the amount of molybdenum plating on the interior of the main tube. The injection tube, shown in greater detail in Figure 2, extends halfway into the 0.45m (1.5ft)-length hot zone. The injection tube is formed by three concentric Pyrex tubes, of inner diameter 4mm, 12mm and 17mm, with the 4-mm tube sealed to the 17-mm tube at the injector tip. Water flows in through the annulus formed by the 4- and 12-mm tubes, and out through the annulus formed by the 12- and 17-mm tubes. Argon gas is introduced between the main tube (25mm) and the 17-mm tube. The reactive gases pass through the innermost (4-mm diameter) tube. The flow pattern thus established keeps most of the molybdenum hexacarbonyl vapor away from the hottest surfaces, where it would thermally decompose to form unneeded products. At the furnace exit, the main tube is connected to an isolation unit where the powder products are collected in tubes constructed of coarse-porosity (P8) filter paper.

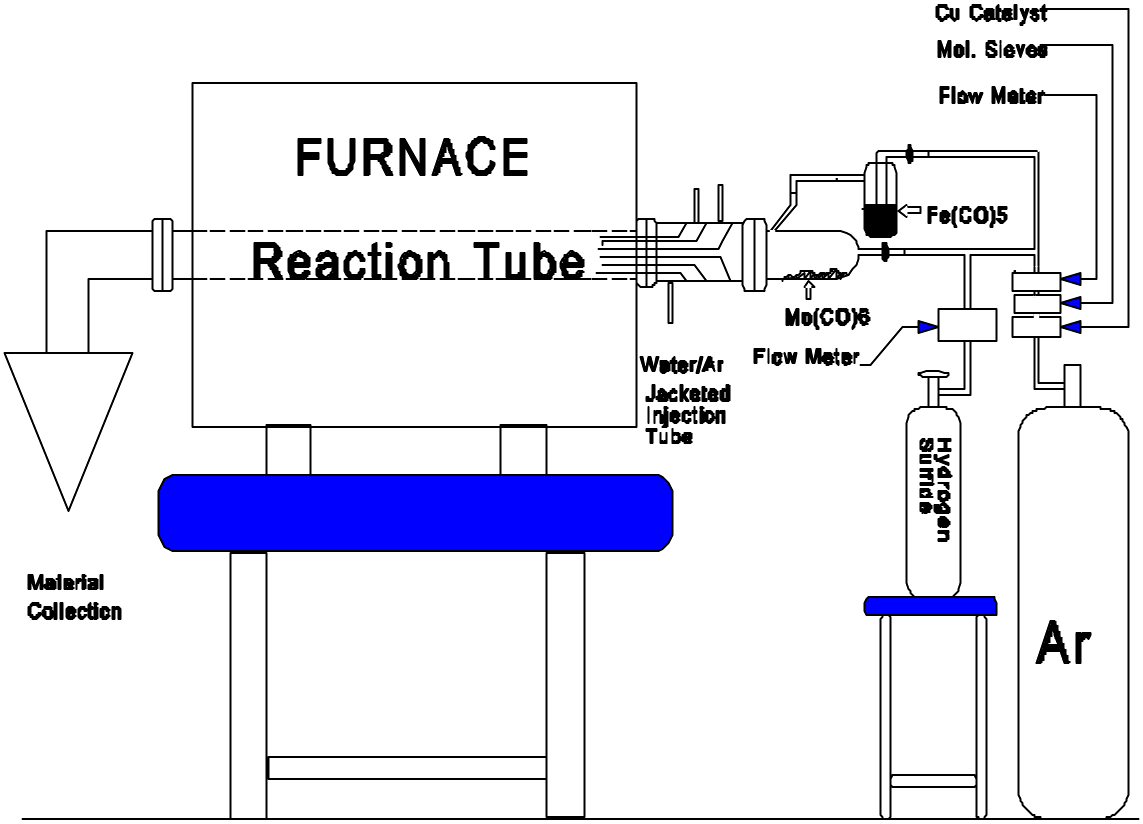

Figure 1. Schematic of apparatus used for synthesis of molybdenum sulfide by vapor-phase reduction of molybdenum carbonyl.

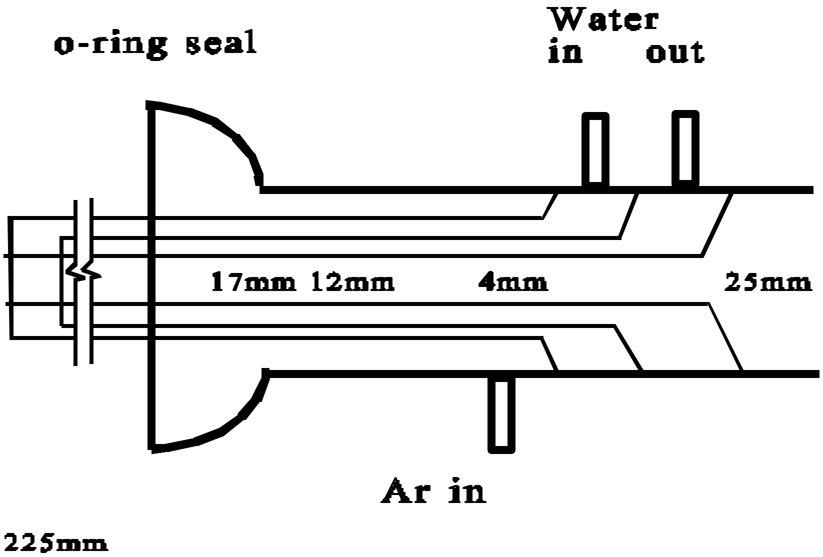

Figure 2. Detail of injector tube cooled by water and argon as used in the apparatus of Figure 1.

Catalytic Reaction Apparatus. The reactor system is shown in Figure 3. The system is extensively controlled by a personal computer (PC), using the commercial software package InTouch by Wonderware. Almost all operating conditions are set directly from the PC, the one exception being the reactor pressure, which must be set manually. Data are logged by the PC at operator-determined intervals. The unit is designed to operate from atmospheric pressure up to 1500psig, and at temperatures up to 500°C.

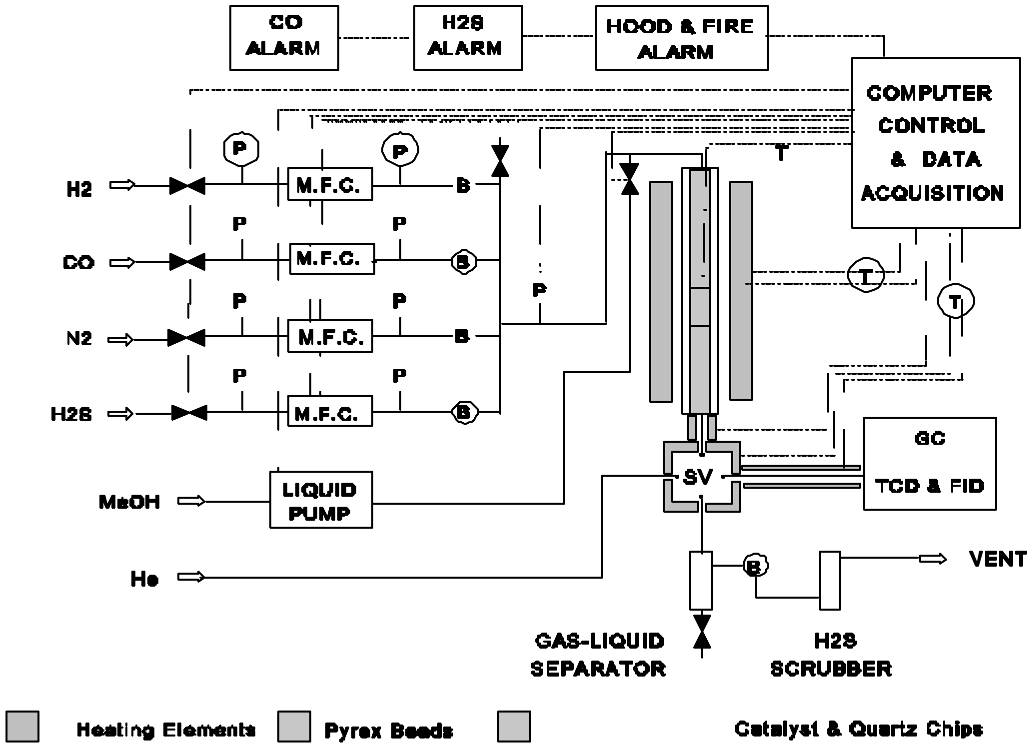

Figure 3. Schematic of apparatus for catalytic reactions. SV, sample valve; MFC, mass flow controller; P, pressure gauge; T, thermocouple; B, back-pressure regulator.

The unit has four lines for gas feed, each independently controlled by a Brooks mass-flow controller, and one line for a liquid feed, using a HPLC pump. (The liquid-feed line was not used in this work.) The reactor is a stainless-steel tube of nominal outer diameter 13mm (0.5 in.) and nominal length 0.6m, placed in a 0.45m (18 in.) single-zone furnace from Applied Test Systems. Typically, 0.5g of catalyst and 3g of crushed quartz are mixed together and placed in the center of the reactor with pyrex beads upstream and downstream of the catalyst-quartz mixture. The product stream is sampled immediately downstream of the reactor using a Valco 6-port gas-sampling valve at the pressure of the reactor and at a minimum temperature of 250 C. Analysis of the products is accomplished on-line by a Hewlett-Packard 5890 gas chromatograph (GC) using two columns and two detectors in parallel. The GC is controlled (using HP Chemstation software) by the same PC in a multitasking MS Windows environment. In the GC, the flow is split between two columns: a HayeSep-DB packed column, 9m x 3.1mm (30ft x 1/8in), and a J&W DBWax capillary column, 20m x 0.1mm ID. The oven temperature for both columns is programmed from 40 to 230 C. The packed column is connected to a thermal conductivity detector (TCD) which provides quantitative analysis for N_2 (an internal standard) as well as CO, CO_2, and H_2O; H_2 is separated but cannot be measured satisfactorily. The capillary column is connected to a flame-ionization detector (FID) and separates all of the C_1-C_5 alcohols, and separates the C_1-C_6 hydrocarbons as a single peak. The reactor effluent that is not passed through the GC is separated by phase. The liquid phase is collected and the vapor phase is vented after passing through an H_2S scrubber.

The entire unit is located in a walk-in hood. The PC monitors alarms for CO and H_2S, and for flows of reactive gases, hood velocity, ambient hood temperature, reactor temperature, reactor pressure, compressed-air supply, and electric power. The unit automatically shuts down in the event of hood failure, fire, power- or air-supply failure, CO or H_2S leak detection, or if gas flows or reactor temperature exceed pre-set operating ranges.

Chemicals. The molybdenum hexacarbonyl, $Mo(CO)_6$, was obtained from Strem Chemical Company and was puried by sublimation prior to use. H_2S for catalyst synthesis was obtained from Matheson Gas Products and was used as received. Blended gases of 4% N_2 in CO and 10% H_2S in H_2 for use in the catalytic pretreatment and reaction were also obtained from Matheson and were also used as received. Other gases were Airco products obtained from West Virginia Welding Supply Company. A commercially available molybdenum sulfide (99% MoS_2) was obtained from Aldrich Chemical Company and used in a few runs for comparison purposes.

Sulfide Synthesis and Characterization. In a typical preparative procedure, 3g $Mo(CO)_6$ in a quartz boat was added to the materials synthesis unit shown in Figure 1 at ambient temperature under flowing inert gas. The isolation unit for product collection unit was then connected to the main tube, and the entire system was purged for 30min. At this point, the flow of H_2S was initiated, and continued for 15-20 min. After the flow of H_2S was stopped, the main tube was heated under a flow of 800-1000 ml/min of inert gas to the desired temperature. At this point, the flow of H_2S was re-started, the water-cooled injection tube was maintained at 85°C with a recirculating water bath, and the tube containing the $Mo(CO)_6$ was heated to 98°C (external temperature) with a heating tape. The reaction was completed after about 2h when all of the $Mo(CO)_6$ had sublimed. The products were collected on P8 coarse-porosity filter paper. Since none of the molybdenum sulfides appeared to be air sensitive, the product was isolated and analyzed in air. A typical yield of product, based on MoS_2, was 90%. Lost material either passed through the filter or deposited on reactor walls.

For characterization studies, the material was used as synthesized. Characterization included N_2 BET surface area measurement, x-ray powder diffraction (XRD) for phase identification, and sulfur composition by combustion analysis. Nitrogen adsorption surface areas were measured with a Coulter Omnisorp 360 instrument, x-ray powder diffraction studies were carried out on a Phillips PW 1800 diffractometer, while sulfur was analyzed with a Leco SC-432DR instrument. Many of these and other measurements have been reported earlier (Close *et al.*, 1995) and will be only briefly described here.

For use as a catalyst in the CO hydrogenation unit, the material was promoted by alkali metals as follows. The acetate salt of the alkali metal and 3ml of methanol were added to nominally 500mg of the sulfide material. The mixture was allowed to dry in air at room temperature. The mixed powder was pressed into a pellet at 4000psi and broken into smaller fragments. The size range 20-40 mesh was used in the catalytic evaluations.

Physically mixing the fine-particle molybdenum sulfide with silica caused the molybdenum powder to disappear into the silica. This "supported" catalyst (more correctly, "diluted" catalyst) was promoted by the following procedure. The acetate was added to nominally 125mg of the sulfide material. This was followed by the addition of 400mg of silica (of surface area $144m^2/g$) and 3ml of methanol. Mixing (grinding), drying, and pressing steps followed as above.

Catalytic Reaction. Pretreatment of the catalyst consisted of temperature-programmed sulfidation followed by hydrogen purging. During the presulfiding, a mixture of 10% H_2S in H_2 was used while the temperature was increased linearly from 200-400°C at a steady rate of 10°C/h, and then held at 400°C for 1h. This was followed by purging in H_2 while the temperature was lowered to 200°C. This pretreatment follows the general procedure used by Duchet *et al.* (1983) for carbon-supported hydrodesulfurization catalysts, except that a slower heating rate was used in the present case. After pretreatment, the system was pressurized to 750psig and the gas flows adjusted to the desired values. Typical values were 25sccm H_2 and 25sccm CO.

The screening reactions reported here were carried out as follows. In all cases, the operating pressure was 750psig. Starting with a reactor temperature of 200°C, the temperature was increased linearly at a steady rate of 10°C/h until the reactor temperature was 400°C. The temperature was then decreased, also at a steady rate of 10°C/h, until the reactor temperature was once again 200°C. The reaction products were typically sampled every 2h and were analyzed by the GC.

Alcohol products in the GC analysis were identified by matching retention times of known standards. Alcohols with up to 4 carbons were identified this way. Linear or methyl-branched alcohols were the predominant products. Hydrocarbons with up to 6 carbons eluted together as the first peak off the GC column. Hydrocarbons with 8 or more carbons were mixed with the alcohol peaks on the GC trace. Any GC peak that was not positively identified as an alcohol was assumed to be a hydrocarbon. This assumption will bias catalytic screening data toward unwanted hydrocarbon products, making conservative the reported rates of alcohol formation.

RESULTS AND DISCUSSION

Characterization: Tables 1 and 2 summarize the characterization of the sulfides prepared by continuous-flow vapor-phase decomposition of molybdenum hexacarbonyl, in terms of the furnace temperature. The other parameters for the synthesis are kept at the "standard" values noted earlier: the temperature of the $Mo(CO)_6$ reservoir, T_{Mo}, at 98°C; the water jacket temperature, T_w , at 85°C, the flow rate of Ar in the innermost (and outermost) tube of the injector, V_i (and V_o), at 220 (and 700) sccm/min.; and the H_2S flow rate, V_{H2S}, at 11 sccm/min.

From Table 1, the sample prepared at 300°C shows a low yield of recovered product, a low surface area, and a poorly crystalline structure. However, the yield of the material increases monotonically with increasing furnace temperature. As summarized in Table 1, the materials prepared at lower temperatures have XRD lines that are characterized by broad bands. For furnace temperatures above 500°C, however, lines of MoS_2 and perhaps S are notable. The surface area measurements of Table 1 indicate that this parameter also increases monotonically with furnace temperature until 500°C. Between 500-700°C, the surface area is essentially constant. However, at higher furnace temperatures, the surface-area values actually decrease. The amount of sulfur in these materials increases with increasing furnace temperature. At 300 and 400°C, the samples are sulfur-deficient, suggesting that oxygen and/or carbon from the $Mo(CO)_6$ is present. Between 500-600°C, the samples are stoichiometric, within error bounds. (The stoichiometric amount of sulfur in MoS_2 corresponds to 40.06wt%.) Samples produced above 500°C show excess sulfur, possibly as elemental S from the thermal decomposition of H_2S.

TABLE 1. EFFECT OF FURNACE TEMPERATURE ON PROPERTIES OF SULFIDE. Other parameters of synthesis apparatus are at "standard" conditions: temperature of $Mo(CO)_6$ reservoir = 98°C, water jacket temperature = 85°C, Ar flow in inner (outer) tube of injector = 220 (700) sccm/min., H_2S flow rate = 11 sccm/min.

T_f [°C]	YIELD	XRD RESULTS (a)	SURFACE AREA [m^2/g]	SULFUR CONTENT [%]	SAMPLE #
300	26.7	5.4	21.4	22.6	2MRC128A
400	45.0	5.6	47.3	22.2	2MRC129A
500	82.7	3.7	76.5	37.9	2MRC115A
600	88.6	2.6	75.4	42.6	2MRC116A
700	95.0	2.1	78.0	46.0	2MRC116C
800	94.6	1.8	72.5	45.6	2MRC118A
900	98.2	1.5	66.2	46.0	2MRC119A

(a) Numbers refer to full width at half height of the x-ray powder diffraction pattern for the (002) peak. Details of the XRD results can be found in Close *et al.* (1995).

The decrease in surface area with increasing furnace temperature (above 700°C, at least) can be understood on the basis of faster grain growth by annealing, and this is consistent with the XRD data as well. However, the increase in surface area with increasing furnace temperature (below 500°C at least) reverses this trend. This anomaly can perhaps be explained by a crystallographic phase modification, from an amorphous material with composition and short-range order corresponding to MoS_2 (at the lowest furnace temperature) to crystalline MoS_2

(above 500°C). This interpretation is also consistent with XPS data on related samples as described by Close *et al.* (1995).

Accordingly, it is reasonable to believe that the material formed at the lowest furnace temperature is an amorphous material with short-range order corresponding to a reduced molybdenum sulfide phase. At higher temperatures, the more crystalline MoS_2 material is formed. At very high furnace temperatures, the material contains crystalline MoS_2 as well as elemental S formed by the decomposition of the H_2S.

The effects of some of the other process variables are summarized in Tables 2 and 3. Increasing the temperature, T_{Mo}, of the molybdenum carbonyl reservoir increases the concentration of molybdenum compound in the vapor phase in the furnace. Hence, larger sizes may be expected. Table 2 shows that the surface area correspondingly decreases but the XRD peaks are somewhat broader, indicating less crystallinity. Increasing the flow rate of inert argon over the reservoir and into the innermost tube of the injector provides less time in the furnace (increases the flux) and may decrease the concentration of molybdenum, if conditions are not in thermodynamic equilibrium in the reservoir. Table 3 shows that the surface area of the product decreases somewhat, but the crystallinity increases.

TABLE 2. EFFECT OF CARBONYL RESERVOIR TEMPERATURE ON PROPERTIES OF SULFIDE.

Other parameters of synthesis apparatus are at "standard" conditions: furnace temperature = 500°C, water jacket temperature = 85°C, Ar flow in inner (outer) tube of injector = 220 (700) sccm/min., H_2S flow rate = 11 sccm/min.

T_{Mo}[°C]	YIELD	XRD RESULTS (a)	SURFACE AREA [m^2/g]	SULFUR CONTENT [%]	SAMPLE #
93	82.8	3.2	95.1	41.3	2MRC113A
98	82.7	3.7	76.5	37.9	2MRC115A
104	82.8	5.7	55.4	32.7	2MRC113B

(a) Numbers refer to full width at half height of the x-ray powder diffraction pattern for the (002) peak. Details of the XRD results can be found in Close *et al.* (1995).

TABLE 3. EFFECT OF CARRIER GAS FLOW ON PROPERTIES OF SULFIDE.
Other parameters of synthesis apparatus are at “standard” conditions: furnace temperature = 500°C, temperature of $Mo(CO)_6$ reservoir = 98°C, water jacket temperature = 85°C, Ar flow in outer tube of injector = 700 sccm/min., H_2S flow rate = 11 sccm/min.

V_i [sccm/min]	YIELD	XRD RESULTS (a)	SURFACE AREA [m^2/g]	SULFUR CONTENT [%]	SAMPLE #
220	82.7	3.7	76.5	37.9	2MRC115A
250	75.5	3.5	64.0	34.1	2MRC115C

(a) Numbers refer to full width at half height of the x-ray powder diffraction pattern for the (002) peak. Details of the XRD results can be found in Close *et al.* (1995).

Catalytic Reactions with Synthesis Gas: The discussion above indicates that intermediate values of the furnace temperature and the cooling rates may represent an optimum flux of molybdenum for synthesis, and an optimum material for a catalyst. Hence the bulk of the reactions of synthesis gas over these materials or their derivatives as catalysts were carried out with the sulfide prepared at a furnace (synthesis) temperature of around 500°C. Most of the catalytic reactions reported below were carried out in the form of temperature-ramped screening tests using synthesis gas with a H_2/CO ratio of around unity and a gas-hourly space velocity of 6 m^3(STP)/kg/h. The (reaction) temperatures were between 200-400°C. In some cases, the temperature cycle was repeated. In every repeat run, the second cycle most nearly reproduced the data obtained from the decreasing-temperature leg of the first cycle.

Figure 4(a) shows a baseline screening run for an unpromoted MoS_2 catalyst, *i.e.*, with no dopants added. The catalyst was made at 500°C with an older-style injector under conditions similar to those used to produce sample 2MRC115A. The space-time yield (STY) of hydrocarbons is excessive. The selectivity to C_2-to-C_4 alcohols is vanishingly small. These results illustrate that unpromoted MoS_2 is not a suitable catalyst for the synthesis of higher alcohols, consistent with the results of Youchang *et al.* (1986).

A similar screening run was carried out using a commercially available sample of molybdenum sulfide. The results can be seen in Figure 4(b). Note the change in scale compared to Figure 4(a). The commercially available molybdenum sulfide shows a smaller production rate of hydrocarbons, and a greater selectivity to C_1-to-C_4 alcohols.

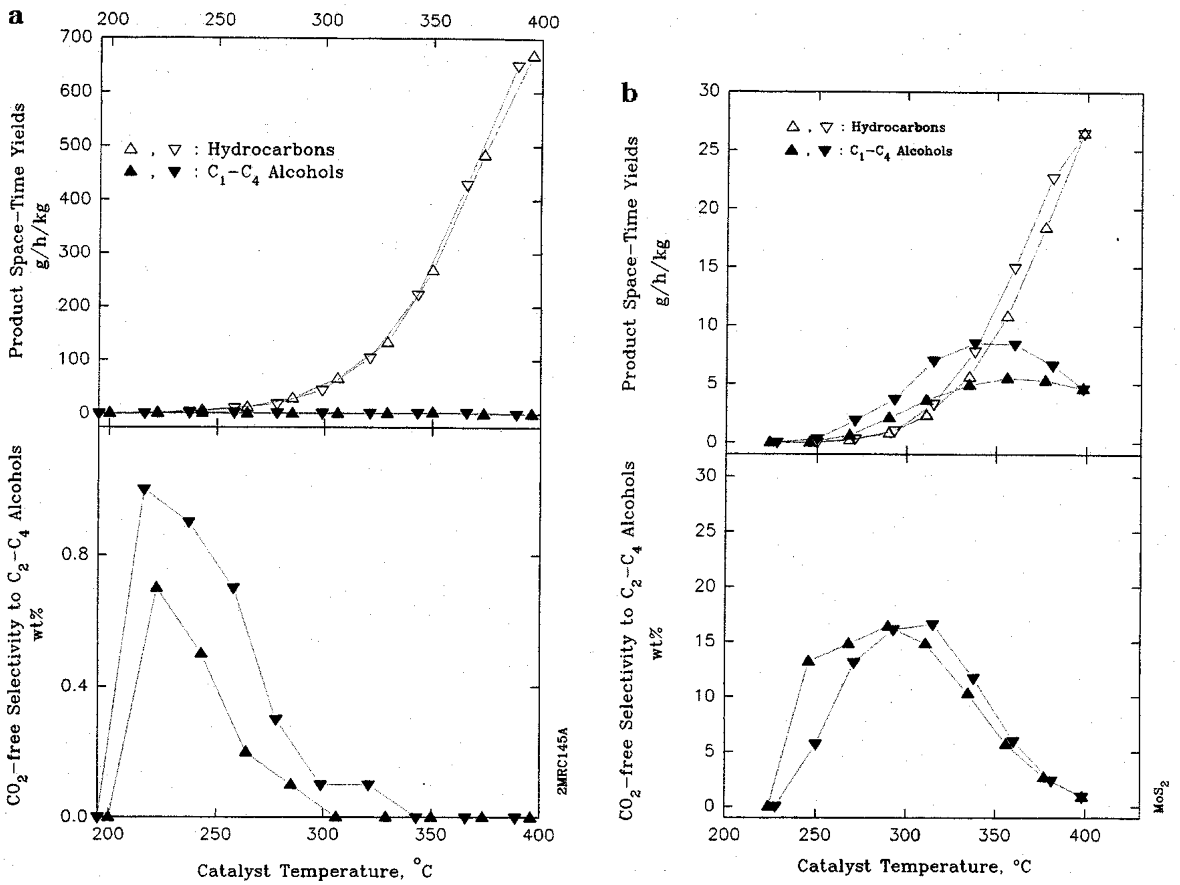

Figure 4.(a) Results of baseline screening run on undoped molybdenum sulfide synthesized by VPR at the "standard" conditions (T_f = 500°C and other conditions of Table I). Reaction conditions: 0.48g catalyst, P = 750psig, GHSV = 6000 l/kg/h, H_2/CO = 1. Upward-pointing and downward-pointing triangles are the data for the temperature-increasing and temperature-decreasing legs respectively. Filled and open symbols refer to alcohols and hydrocarbons respectively.(b) Results of baseline screening run on commercially available molybdenum sulfide. Symbols and reaction conditions are as in (a) except that 0.50g catalyst was used.

Figure 5 illustrates the beneficial effect of alkali promotion. The sulfide was synthesized at 500°C, as was the catalyst used in Figure 4(a), but now potassium has been added such that K/Mo = 0.7. At intermediate temperatures, the STY of C_1-to-C_4 alcohols greatly exceeds that of hydrocarbons. Further, selectivities to C_2-to-C_4 alcohols are appreciable. Qualitatively similar improvements upon alkali promotion were found when using the commercially available molybdenum sulfide in a screening run. Similar effects have been reported by other workers using other molybdenum sulfide catalyst preparations (Youchang *et al.*, 1986, Murchison *et al.*, 1988).

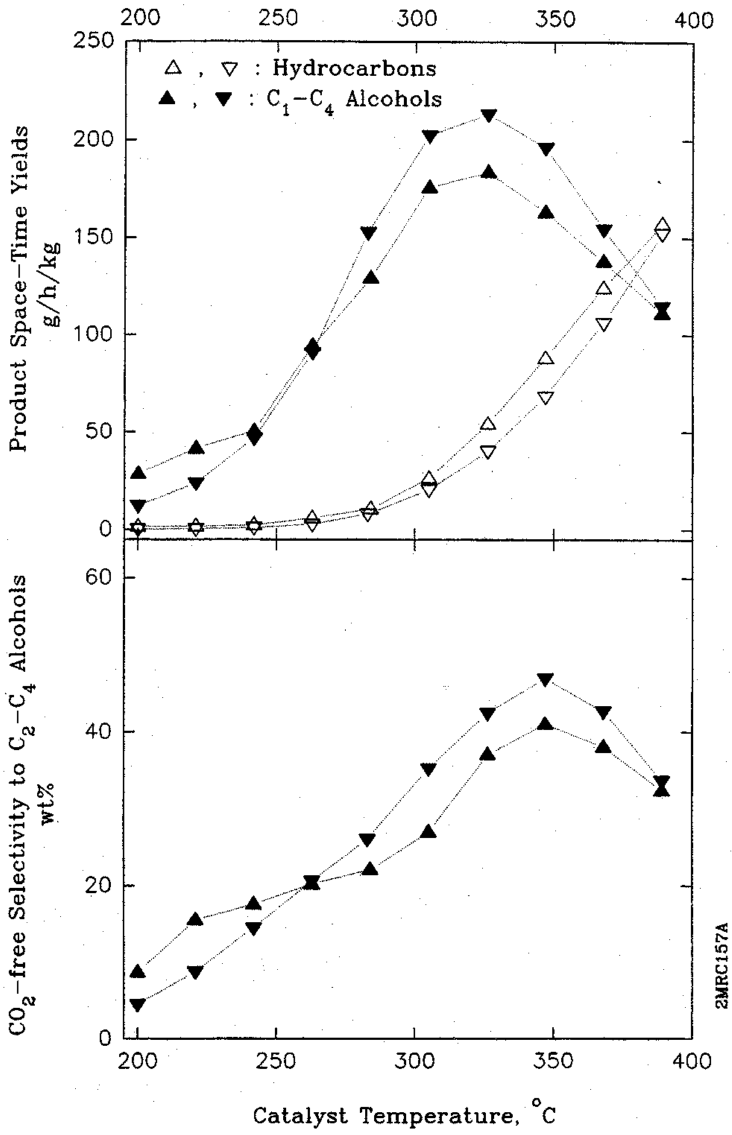

Figure 5. Results when the molybdenum sulfide of Figure 4a is doped with potassium (K/Mo = 0.7). Reaction conditions are as in Figure 4a except that the weight of catalyst used is 0.53g. Symbols are as in Figure 4a.

Figure 5 exhibits the four features typical of the temperature-dependence of the catalytic performance of alkali-doped molybdenum sulfides prepared in this fashion -- a monotonic increase in the STY of hydrocarbons with temperature (also seen in Figures 4a and 4b); a maximum for the STY of C_1-to-C_4 alcohols; a maximum (corresponding to a higher temperature) for the CO_2-free selectivity towards C_2-to-C_4 alcohols; and an improvement in performance with respect to these three parameters after the catalyst has been run at 400°C. It is worth noting that, while the molybdenum sulfide has already been exposed to 400°C during pretreatment with 10% H_2S in H_2, it still changes at 400°C under reaction conditions.

Figure 6 shows the product distribution of alcohols measured under decreasing temperature conditions for the screening run illustrated in Figure 5. The effect of temperature on product distribution shows that the (CO_2-free) selectivity to methanol monotonically decreases with increasing temperature, while that to the hydrocarbons monotonically increases. The selectivity to C_2-to-C_4 alcohols passes through a maximum around 350°C (as also shown in Figure 5). Among the higher alcohols, it can be seen that ethanol comprises the largest fraction, in the temperature range of interest. The amount of ethanol in the alcohol fraction passes through a maximum around 370°C. The maximum point corresponds to the point of steepest rise for the propanol fraction, while butanol is smallest but increasing. Figure 6 is consistent with a sequential formation of higher alcohols, with methanol converting to ethanol and thence to propanol and butanol, in turn, as noted by Santiesteban *et al.* (1988) and others.

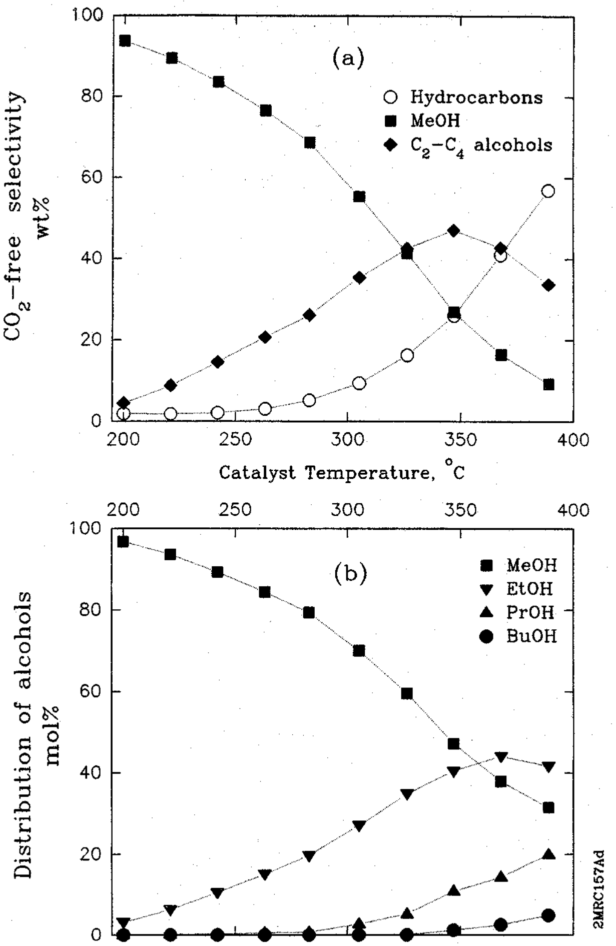

Figure 6. Selectivities of the K-doped molybdenum sulfide catalyst of Figure 5.

The effect of the nature of the alkali dopant is shown in Figure 7, where we compare doping with K, Rb and Cs, each to a molar ratio of 0.7, as before. The molybdenum sulfide was prepared at 500°C, as before. The same qualitative features are found for each dopant. The Cs-doped material has the lowest STY of C_1-to-C_4 alcohols, and the lowest selectivity to C_2-to-C_4 alcohols, and is also least affected by reaction at 400°C. The K-doped material has the highest selectivity to C_2-to-C_4 alcohols, but the K- and the Rb-doped materials are virtually indistinguishable in terms of their total alcohol STY's at all temperatures considered. The performances of both the K- and the Rb-doped material improve appreciably after reaction at the highest temperature. There are no appreciable changes in the optimal temperatures for formation rate and for selectivity with changes in the alkali metal after the high-temperature reaction.

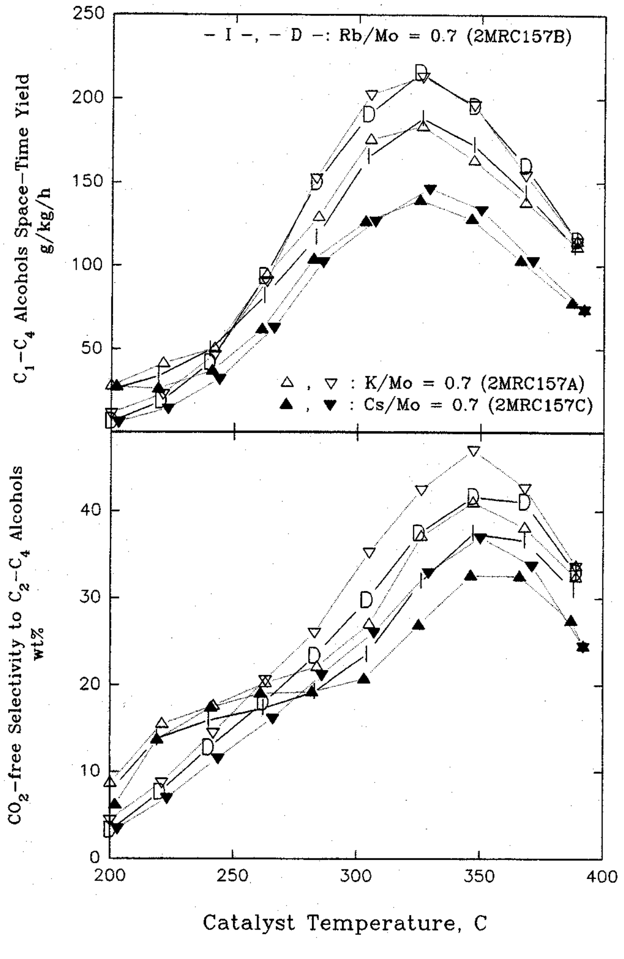

Figure 7. Catalytic performances of the molybdenum sulfide catalyst of Figure 4a when doped with various alkali metals. (Alkali/Mo = 0.7).Symbols used for increasing-temperature and decreasing-temperature legs respectively: K-doped, open upward triangle, open downward triangle; Rb-doped, I, D; Cs-doped, filled upward triangle, filled downward triangle. Amounts of catalysts used: K-doped, 0.53g; Rb-doped, 0.51g; Cs-doped, 0.51g. Other reaction conditions are as in Figure 4a.

Figure 8, when compared with Figure 7, shows the effect of changing the concentration of the alkali dopant. At the lower value of the Cs/Mo ratio (0.22, Figure 8), there are marked and favorable changes in the STY of C_1-to-C_4 alcohols (increases), the hydrocarbon STY (decreases), and the values of these parameters after reaction at the highest temperatures. However, the selectivity to C_2-to-C_4 alcohols is not significantly affected, and the optimum temperature for selectivity appears to decrease, approaching the optimum temperature for the alcohol STY. The promoter level of 0.22 was recommended by Klier *et al.* (1988b) as the optimum value for Cs promotion. The improved performance at this ratio is confirmed by this study.

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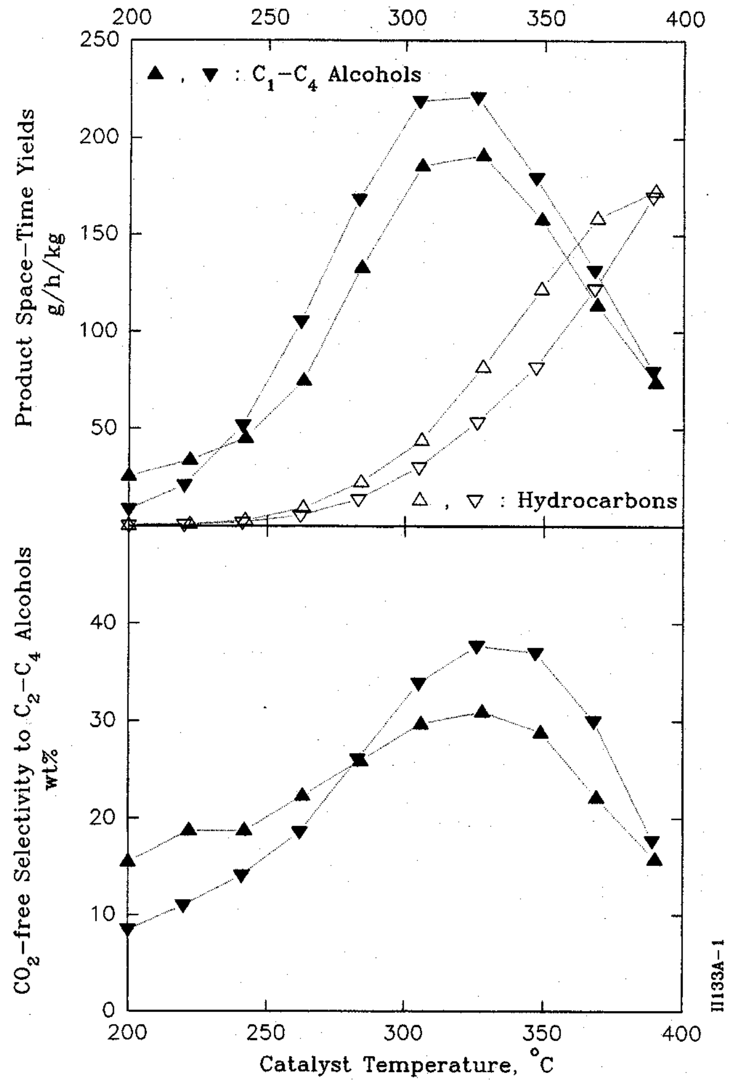

Figure 8. Catalytic performance of the alkali-doped molybdenum sulfide when Cs/Mo = 0.22. Symbols and reaction conditions are as in Figure 4a. Amount of catalyst used is 0.4g.

It is worth comparing Figure 8 with Figure 9, which is similar except that the sulfide was synthesized at a furnace temperature (T_f) of 400°C. From Table 1, this material has a smaller surface area and a less-crystalline structure than the sulfide in Figure 8, for which T_f = 500°C. However, there is relatively little difference between the two catalysts, except that Figure 8 exhibits perhaps a somewhat greater STY of C_1-to-C_4 alcohols. However, the selectivity towards C_2 - C_4 alcohols is similar, implying perhaps a somewhat greater production of methanol.

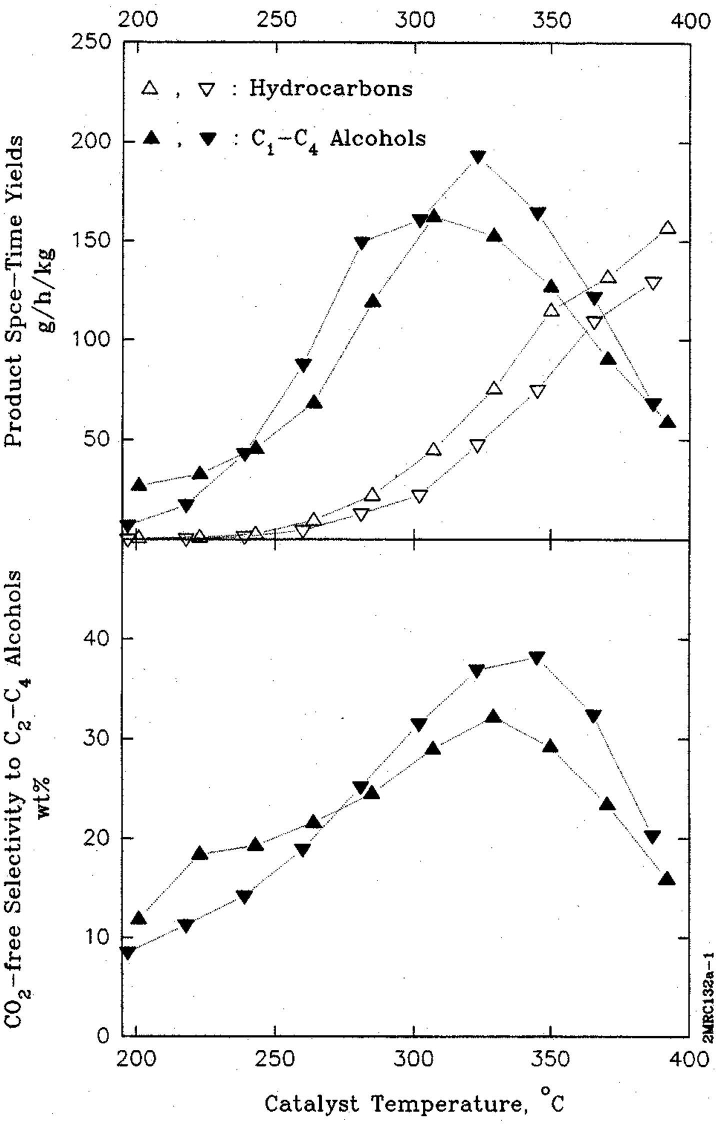

Figure 9. Performance of Cs-doped catalyst similar to that in Figure 8, except that the molybdenum sulfide was synthesized at a furnace temperature, T_f, of 400°C (Sample 2MRC129A in Table I).

Analogously, Figure 10 can be compared with Figure 5 for the case of the K-doped catalysts. The sulfide of Figure 10 was synthesized at T_f = 600°C, and has a better-developed crystalline structure but approximately the same surface area as that of Figure 5 (for which T_f = 500°C). The maximum selectivity towards C_2 - C_4 alcohols and the maximum STY of C_1-to-C_4 alcohols is greater in Figure 5. Further, the optimum temperatures for these two parameters are greater in Figure 10 than in Figure 5. Hence, there would appear to be a slight incentive towards using the sulfide prepared at T_f = 500°C as the basis of the catalyst for the synthesis of higher alcohols.

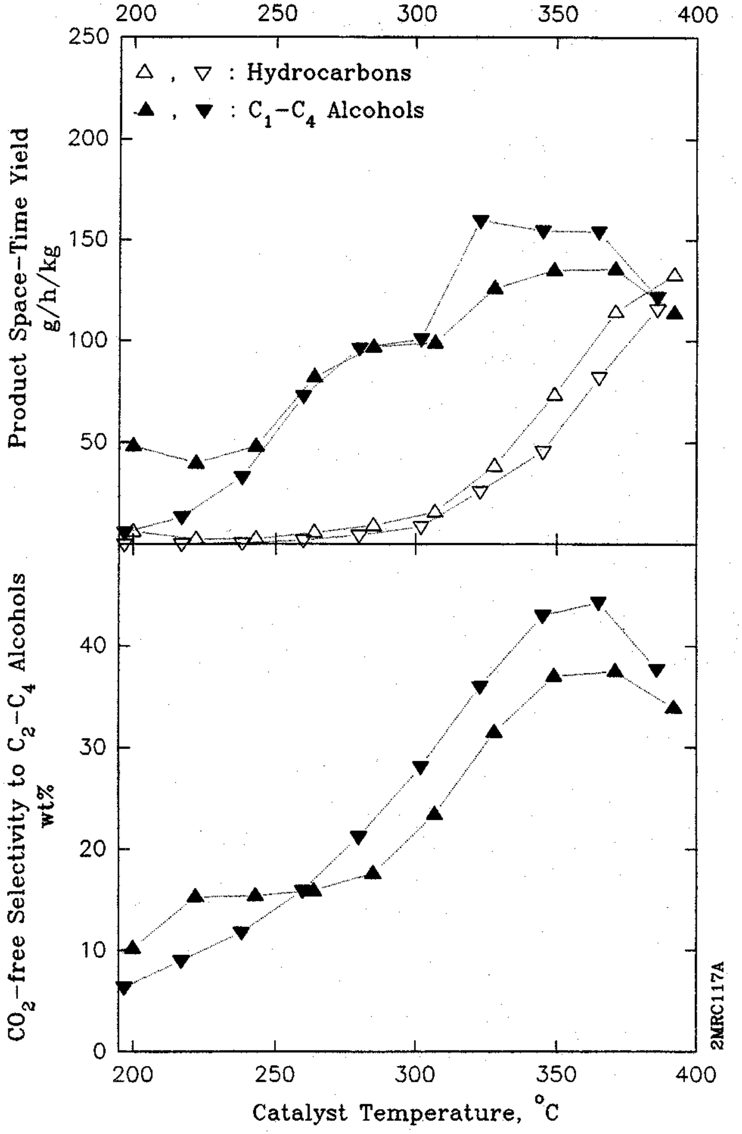

Figure 10. Performance of K-doped catalyst similar to that in Figure 5 except that the molybdenum sulfide was synthesized at a furnace temperature, T_f, of 600°C.

Figure 11 illustrates the effect of introducing the silica diluent to a K-doped catalyst. Comparing these curves with those of Figure 5, we note decreases in the maximum STY of C_1-to-C_4 alcohols (from 200 to 120 g/h/kg catalyst) and the corresponding hydrocarbon STY(from 40 to 20 g/h/kg catalyst), and a sharp decrease in the selectivity of C_2 - C_4 alcohols (from 47 to

33%). The decreases in the STYs must take into consideration that the mass of Mo per mass of catalyst has decreased in the diluted catalyst, from a loading of 41.9% Mo in Figure 5 to 13.6% Mo in Figure 11. On a molybdenum basis, using the silica results in an increase in the maximum alcohol STY from 477 to 882 g/h/kg Mo, but also results in an increase in the corresponding hydrocarbon STY from 95 to 147 g/h/kg Mo. In this regard, it should be pointed out that the sulfides used for the two catalysts are not identical: that for the unsupported catalyst corresponded to a synthesis T_f of 500°C, while that for the diluted catalyst corresponded to a synthesis T_f of 400°C. However, considering that the results of Figure 8 and 9 were not markedly different, it would appear that the changes noted between Figures 5 and 11 can be ascribed more to the introduction of the silica than to the slightly different sulfide material used.

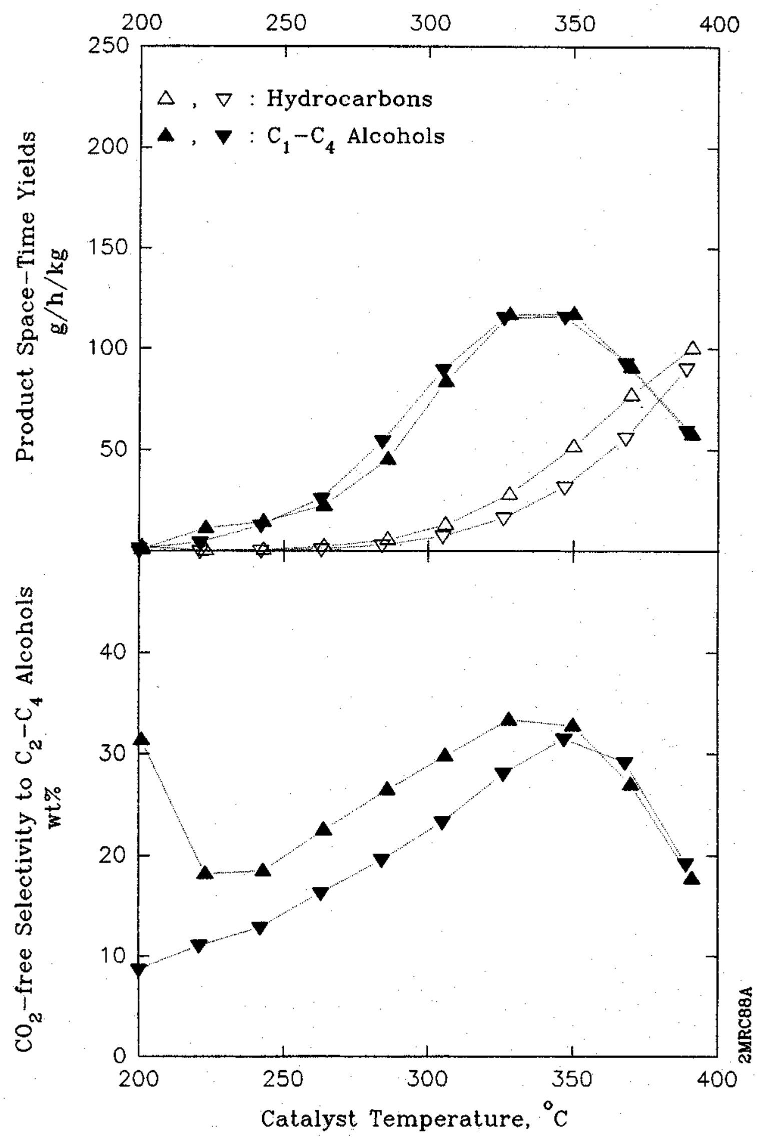

Figure 11. Performance of K-doped catalyst essentially similar to that in Figure 5 after dilution with silica. Symbols as in Figure 4a.

Other synthesis parameters exhibit less of an effect on the catalytic properties than does the furnace temperature, T_f. For example, consider the role of the Mo reservoir in Figure 1. Samples 2MRC113A and 2MRC113B described in Table 2 were doped with potassium (K/Mo = 1) and diluted with silica to correspond to a loading of 25.5% Mo. Runs using these materials as catalysts yielded virtually identical results, with a maximum STY of C_1-to-C_4 alcohols of 160g/h/kg catalyst (at 320°C), a corresponding hydrocarbon STY of 20g/h/kg, and a maximum selectivity to C_2 - C_4 alcohols of 40% (at 350°C).

In summary, the results indicate that molybdenum sulfide prepared by vapor-phase reaction at a furnace temperature of 500 C (and other standard conditions of Table 1) and promoted by an alkali metal to a value of the alkali/Mo ratio of 0.7 is a suitable catalyst for the synthesis of higher alcohols. This catalyst was considered in Figures 5-7.

SUMMARY AND CONCLUSIONS

Vapor-phase synthesis yields molybdenum sulfide materials with consistent structures and in sufficient yields to be suitable for the production of catalysts for higher-alcohol synthesis. These materials have been characterized by XRD, elemental analysis and BET surface area, and show distinct trends which can be correlated with the parameters of the synthesis process used. While the molybdenum sulfides themselves are inactive for the formation of higher alcohols, doping these sulfides with alkali results in materials which can be used for this purpose.

These materials, both unsupported as well as diluted with silica, have been used in a plug-flow microreactor operated in a screening mode, *i.e.*, by increasing the temperature gradually from 200°C to 400°C and back again to 200°C, with synthesis gas having a H_2/CO ratio of unity. In all cases, the main alcohols formed are straight-chain compounds, containing from one to four carbon atoms, and with the -OH group at a terminal carbon atom. Methanol is formed in the greatest amounts at low temperatures, while ethanol is formed and passes through a maximum at intermediate temperatures; propanol and butanol increase monotonically with temperature in the range considered here.

Changing the nature of the sulfide in the catalyst leads to at best small changes in the catalytic performance. Using a furnace temperature of 500°C in the synthesis procedure appears to result in an acceptable material.

The alkali metals used, K, Rb and Cs, all appear to have similar promoting effects. At an alkali/Mo ratio of 0.7, the performances of K and Rb are superior to those of Cs. For Cs, the performance can be improved by decreasing the ratio from 0.7 to 0.22.

Maxima with respect to temperature are observed both for the space-time yields (STYs, amounts/time/mass catalyst) of C_1-to-C_4 alcohols and for selectivity towards C_2 - C_4 alcohols. The optimum temperature for selectivity is generally higher than that for the STY. Hence, by varying the temperature, and the type and amount of the alkali metal, optimum conditions for the STY or selectivity can be achieved.

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REFERENCES

Badische Anilin and Soda Fabrik. *D.R. Patent 293,787*, 1913.

Chatzitheodorou, G.; Fiechter, S.; Kunst. M.; Luck, J.; Tributsch, H. Thermochemical Preparation of Semiconducting Transition-Metal Chalcogenide Films for Energy Conversion and Storage, Lubrication and Surface Protection. *Mater. Res. Bull.* **1988**, *23*, 1261.

Close, M.R.; Petersen, J.L.; Kugler, E.L. Synthesis and Characterization of Nanoscale Molybdenum Sulfide Catalysts by Controlled Gas-Phase Decomposition of $Mo(CO)_6$ and H_2S. Submitted for publication in *Inorganic Chem.*

Duchet, J. C.; van Oers, E. M.; de Beer, V. H. J.; Prins, R. Carbon-Supported Sulfide Catalysts. *J. Catal.* **1983**, 80, 386.

Eggertsen, F.T.; Roberts, R.M. MoS_2 of High Surface Area. *J. Phys. Chem.* **1959**, *63*, 1981.

Kinkade, N.E. Eur. Pat. Appl. 84116467.6. Assigned to Union Carbide Corp. December 28, 1984.

Klier, K.; Herman, R.G.; Simmons, G.W.; Lyman, C.E.; Santiesteban, J.G.; Najbar, M.; Bastian, R. *Direct Synthesis of Alcohol Fuels over Molybdenum-Based Catalysts.* Final Technical Report, DOE/PC/80014-T1, U.S. Department of Energy, Contract No. DE-AC22-85PC80014; Lehigh University, Bethlehem, PA, 1988a.

Klier, K.; Herman, R.G.; Nunan, J.G.; Smith, K.J.; Bogdan, C.E.; Young, C.-W.; Santiesteban, J.G. Mechanism of Methanol and Higher Oxygenate Synthesis. In *Methane Conversion*; Bibby, D.M., Chang, C.D., Howe, R.F., Yurchak, S., Eds.; Elsevier: Amsterdam, 1988.

Lee, J.S.; Kim, S.; Lee, K.H.; Nam, I.-S.; Chung, J.S.; Kim, Y.G.; Woo, H.C. Role of Alkali Promoters in K/MoS_2 Catalysts for $CO-H_2$ Reactions. *Applied Catalysis A*, **1994**, *110*, 11.

Lox, E.S.; Froment, G.F. Kinetics of the Fischer-Tropsch Reaction on a Precipitated Promoted Iron Catalyst. 2. Kinetic Modeling. *Ind. Eng. Chem. Res.* **1993**, *32*, 71.

Murchison, C.B.; Conway, M.M.; Stevens, R.R.; Quarderer, G.J. Mixed Alcohols from Syngas over Moly Catalysts. In *Proc. 9th Intern. Congr. Catal., Calgary, Canada*; Phillips, M.J., Ternan, M., Eds.; The Chemical Institute of Canada: Ottawa, **1988**, *2*, 626.

Oyama, T.; Ishii, T.; Takeuchi, K. *Kazuo Reza Kenkyu* **1994**, *22*, 2.

Oyama, T.; Takehisa, K.; Ishii, T.; Takeuchi, K. *Reza Kagaku Kenkyu* **1989**, *11*, 90.

Ponec, V. Active Centers for Synthesis Gas Reactions. *Catalysis Today* **1992**, *12*, 227.

Rice, D.A.; Hibble, S.J.; Almond, M.J.; Mohammad, K.A.H.; Pearse, S.P. Novel Low-Temperature Route to Known (MnS and FeS_2) and New (CrS_3, MoS_4 and WS_5) Transition-Metal Sulfides. *J. Mater. Chem.* **1992**, *2*, 895.

Santiesteban, J.G.; Bogdan, C.E.; Herman, R.G.; Klier, K. Mechanism of C_1-C_4 Alcohol Synthesis over Alkali/MoS_2 and Alkali/Co/MoS_2 Catalysts. In *Proc. 9th Intern. Congr. Catal., Calgary, Canada*; Phillips, M.J., Ternan, M., Eds.; The Chemical Institute of Canada: Ottawa, **1988**, *2*, 561.

Smith, K.J.; Herman, R.G.; Klier, K. Kinetic Modelling of Higher Alcohol Synthesis over Alkali-Promoted Cu/ZnO and MoS_2 Catalysts. *Chem. Eng. Sci.* **1990**, *45*, 2639.

Suhr, H.; Schmid, R.; Traus, I. *D.E. Patent 3834356*, Assigned to Schering A.-G., April 12, 1990.

Youchang, X.; Naasz, B.M.; Somorjai, G.A. Alcohol Synthesis from CO and H_2 over Molybdenum Sulfide. *Applied Catalysis*, **1986**, *27*, 233.

Wildervanck, J.C.; Jellinek, F.Z. *Z. Anorg. Allgem. Chem.* **1964**, *328*, 309.