ABSTRACT

The objective of this research was to investigate sulfur-resistant catalysts for the conversion of synthesis gas having $H_2/CO \leq 1$ into C_1-C_4 alcohols, especially ethanol, by a highly selective and efficient pathway, while also promoting the water gas shift reaction. The catalysts chosen are bifunctional, base-hydrogenation, sulfur-tolerant transition metal sulfides with a heavy alkali, e.g. Cs^+, promoter dispersed on their surfaces. The combination of the two functions also greatly promotes the water gas shift reaction (WGSR), and the catalyst can also be used as a low temperture, sulfur-tolerant WGSR catalyst.

The modes of activation of H_2 and CO on MoS_2 and alkali-doped MoS_2 were considered, and computational analyses of the thermodynamic stability of transition metal sulfides and of the electronic structure of these sulfide catalysts were carried out. It was shown that among the sulfides, MoS_2, WS_2, ReS_2, and RuS_2 have a balance in reducibility and oxidizability and should be the most stable catalysts under higher alcohol synthesis conditions. Theoretical studies of the electronic character of MoS_2 were carried out, which centered on the orbital composition of the MoS_2 valence band, obtained experimentally by X-ray photoelectron spectroscopy. It was shown that the covalent nature of MoS_2 arise from a large amount of mixing between the S 3p orbitals and the Mo $4d_z2$, $4d_x2$-$_y2$, and $4d_{xy}$ orbitals.

In the preparation of the cesium-promoted MoS_2 catalysts, a variety of preparation methods using CsOOCH were examined. Among the catalysts prepared and tested were 10, 13, and 20 wt% CsOOCH/MoS_2 materials. These catalysts were tested for alcohol synthesis activity and selectivity from $H_2/CO = 1$ synthesis gas at 8.1 MPa in the range of temperatures of 245-350°C. The gas hourly space velocity (GHSV) of the reactant mixture was typically maintained at ≈7,800 ℓ/kg cat/hr. It was shown that testing freshly prepared catalysts protected from air exposure was crucial to obtaining highly active catalysts. This was conveniently achieved by carrying out the doping procedure, e.g. with the 10 wt% CsOOCH-doped molybdenum disulfide, in a vacuum apparatus. X-Ray powder diffraction studies demonstrated that prolonged air exposure of CsOOCH-doped catalysts led to segregation and agglomeration of the CsOOCH component to form crystalline CsOOCH on the surface of the MoS_2 catalyst. In all cases, doping with CsOOCH led to a lost of surface area.

The undoped molybdenum disulfide catalyst only produced hydrocarbons. Injection of methanol to the synthesis gas demonstrated that homologation did not occur over the undoped MoS_2 sample, but the methanol was completely dissociated. In contrast, Cs-doped MoS_2 catalysts all produced linear alcohols, along with smaller amounts of hydrocarbons. The selectivity toward hydrocarbons generally increased with increasing reactor temperature. However, testing of a 10 wt% CsOOCH/MoS_2 catalyst progressively to temperatures as high as 350°C led to partial deactivation of the catalyst. Upon sequentially testing the catalyst again during which a progressive temperature programming of 265-340°C was utilized, the selectivity pattern was reversed from that of the fresh catalyst, i.e. the alcohol synthesis selectivity increased with increasing reaction temperature rather than decreased. The causes of this behavior need to be investigated further.

With a 20 wt% $CsOOCH/MoS_2$ catalyst, temperature, pressure, and flow rate dependences of the synthesis reactions were investigated in the presence and absence of H_2S in the $H_2/CO = 1/1$ synthesis gas during short term testing experiments. The temperature seemed to produce the largest effect on alcohol yield and on the hydrocarbon selectivity, with both increasing with increasing temperature. The presence of 45.5 ppm H_2S in the synthesis gas did increase the C_2^+ alcohol/methanol molar ratio at 285°C, but this effect was not noticeable at higher temperatures under the reaction conditions that were employed. On the other hand, the presence of H_2S decreased the yield of methane at high temperatures (340-350°C), but this effect was not noticeable at lower temperatures. At high temperature and pressure (350°C and 10.3 MPa) with 45.5 ppm H_2S in the synthesis gas, increased gas hourly space velocity of the synthesis gas reactant significantly decreased the yield of methane, while affecting the yield of alcohols to a much lesser extent.

It was shown that with a carefully prepared 10 wt% $CsOOCH/MoS_2$ catalyst, reproducible and high alcohol synthesis activity could be obtained. For example, at 295°C with $H_2/CO = 1$ synthesis gas at 8.3 MPa and with GHSV = 7760 ℓ/kg cat/hr, the total alcohol space time yield was ≈300 g/kg cat/hr (accompanied with a hydrocarbon space time yield of ≈60 g/kg cat/hr). Over a testing period of ≈130 hr, no net deactivation of the catalyst was observed.

A K/MoS_2 catalyst was prepared by intercalation of metallic potassium from liquid NH_3 into MoS_2 under vacuum. Long term testing demonstrated that this catalyst was active toward alcohol synthesis, and ≈115 g of alcohols/kg cat/hr were produced at 295°C. However, its overall behavior was not different from the conventionally prepared catalysts using impregnation of salts.

INTRODUCTION

Utility and Synthesis of Oxygenates for Fuels

The 1990 amendments to the U. S. Clean Air Act focused attention on the development of reformulated gasoline (RFG), which aims to reduce volatile organic compounds (VOC) and toxic and/or carcinogenic compounds and to reduce resultant emissions of carbon monoxide and nitrogen oxides. The performance standards for 1995 for RFG includes 15% reduction in VOC and toxic emissions and that the fuel contain not more than 1.0% benzene and 25% aromatics, no increase in nitrogen oxide emissions, and a minimum of 2.0 wt% oxygen [1]. Most recently, the Renewable Oxygenate Standard that has been considered requires that 30% of the oxygen contained in RFG be derived from a renewable source, i.e. ethanol produced by fermentation of biomass [2]. The way to add oxygen to gasoline is through ethers or alcohols. There have been some problems associated with adding alcohols directly to gasoline, but most of these have been overcome. A problem that is usually pointed out is that a phase separation of the fuel can occur, particularly with methanol/gasoline mixtures when water is present. A second problem is that addition of alcohols increases the Reid vapor pressure, therefore increasing the VOC, but the magnitude of increase is significantly less than that observed for butane. However, an overall decrease in fuel vapor pressure is one of the goals of the Clean Air Act. Because the ethers compensate for the loss of octane number due to reduction of aromatics, have about the same density as gasoline, reduce the vapor pressure of the gasoline, and provide some reduction in the emission of carbon monoxide from vehicles, they have been the focus of much research [3] and are compared with some C_1-C_5 alcohols in Table 1.

TABLE 1
Selected Properties of Hydrocarbon Fuels and Oxygenated Additives

Oxygenate (or Fuel)	Boiling Point (°C)	Density (g/ml)	Blending RVP[a] (psi)	Oxygen Content (wt%)
MIBE	58	0.7424		18.2
MTBE	55	0.75[b]	8	18.2
ETBE	73	0.74	4	15.7
IPTBE	87	0.76	2.5	13.8
DIPE	68	0.73	5	15.7
TAME	86	0.77	1-1.5	15.7
TAEE	101	0.77	1	13.8
Methanol	65	0.7946	31⁺	50.0
Ethanol	78	0.7898[c]	18	34.8
i-Propanol	82	0.7855	14	26.7
1-Butanol	118	0.8098		21.6
i-Butanol	108	0.80	5	21.6
t-Butanol	83	0.7887	9	21.6
t-Amyl alcohol	102	0.81	6	18.2
Butane	-0.5	0.5788	55[d]	0.0
Gasoline	38-204	0.72-0.78	---	----
Diesel Fuel	163-399	0.83-0.88	---	----

[a] Reid vapor pressure (RVP) values are mainly from Piel, W. J., "*Proc. 1st Biomass Conf. of Americas,*" Burlington, VT (1993).

[b] Equivalent to 6.2 lb/gal.

[c] Equivalent to 6.6 lb/gal.

[d] From Guetens, Jr., E. G., DeJovine, J. M., and G. J. Yogis, Hydrocarbon Proc., 61(5), (1982).

The principal ethers that are produced on a commercial scale are methyl tertiarybutyl ether (MTBE) and tertiaryamyl methyl ether (TAME). Ethyl derivatives of these are ETBE and TAEE. Other ethers include methyl isobutyl ether (MIBE), isoproply tertiarybutyl ether (IPTBE), and diisopropyl ether (DIPE). Early attention was focused on MTBE, but in light of the considered Renewable Oxygen Standard, the focus tended to shift to ethyl tertiarybutyl ether (ETBE) [4]. In these processes, methanol for MTBE or ethanol for ETBE and isobutene, obtained as a side-product of petroleum refining, are passed over an acid resin catalyst to produce the ethers. In the past few years, much research was focused on the synthesis of new fuel-grade ethers by new pathways. These include syntheses from alcohols, which can be synthesized from coal-derived H_2/CO synthesis gas and then passed over acid catalysts, such as Nafion or Amberlyst [5,6,7,8,9]. However, with relatively inexpensive natural gas and petroleum, the research emphasis has shifted again to the synthesis of higher alcohols because greater space time yields are required for commercially feasible processes. For the synthesis of ethers from alcohols derived from CO_2-free synthesis gas, the slow synthesis step of the entire process is the formation of higher alcohols, i.e. the $C_1 \rightarrow C_2$ carbon chain growth step. The process of forming C_5 ethers from alcohols calls for the formation of methanol and isobutanol in comparable amounts from CO_2-free synthesis gas using Cs/Cu/ZnO- and Cs/MoS_2-based catalysts. The alcohols could then be passed over sulfated zirconia to selectively dehydrate isobutanol to isobutene [10], with the methanol and isobutene then being passed over other acid catalysts to form the ether, as mentioned earlier.

There are three classes of catalysts used for higher alcohol synthesis (HAS). These consist of:

1. Modified high pressure methanol synthesis catalysts, such as alkali-doped ZnO/Cr_2O_3.
2. Modified low pressure methanol synthesis catalysts, such as alkali-doped $Cu/ZnO/Al_2O_3$.
3. Modified Fischer-Tropsch or methanation catalysts, such as alkali-doped $CuO/CoO/Al_2O_3$ or alkali-doped MoS_2.

Of the catalysts mentioned above, the alkali-doped molybdenum disulfide is the least studied and the least understood, although it has been shown to produce significant quantities of linear alcohols [11-14]. Therefore, the present research project was centered on synthesizing and testing a number of alkali-promoted metal sulfide catalysts for the synthesis of C_1-C_4 alcohols. The Introduction of this report considers carbon monoxide and hydrogen activation, carbon-carbon bond formation and chain growth, and the proposed active sites for each process over the molybdenum disulfide catalyst. The role of the alkali promoter will be discussed, as will be the roles of molybdenum and sulfur in the mechanism of higher alcohol synthesis. For a more complete history of higher alcohol synthesis and a review of various alcohol synthesis mechanisms, the interested reader is referred to Reference [11].

Molybdenum Disulfide Catalysts

Molybdenum disulfide-based catalysts are used for hydrodesulfurization, hydrodenitrogenation, hydrorefining, and hydrocracking. In 1984, it was discovered that alkali-doped MoS_2 produces alcohols from hydrogen-deficient H_2/CO synthesis gas [12-14]. This catalyst has been shown to be sulfur-resistant, unlike other HAS catalysts that are being developed, such as the Cu/ZnO-based catalysts [15]. This is highly desirable for industrial processes because coal-derived synthesis gas contains sulfur. In addition, iron carbonyl, which is produced in steel lines containing high pressures of carbon monoxide, apparently does not adversely affect the activity of the alkali/MoS_2. The distribution of products formed, including both alcohols and hydrocarbons, over these catalysts follow Anderson-Schultz-Flory distribution of products.

Structure of Molybdenum Disulfide

Molybdenum disulfide exists in two morphologies, hexagonal and rhombohedral. The hexagonal form (a = 3.16 Å, c = 12.19 Å), which is written as 2H-MoS_2, is the morphology present in these catalytic systems and is shown in Figure 1. The rhombohedral form (a = 3.16 Å, c = 18.38 Å), written as 3R-MoS_2, is represented in Figure 2. The rhombohedral form is obtained at high pressure, greater than 47 kbar, and at temperatures above 1050°C, and its catalytic properties have not been extensively studied. Molybdenum disulfide in the hexagonal form can be found in nature as the mineral molybdenite. Molybdenite has a layered structure in which Mo is in the +4 oxidation state and is coordinated to six sulfur anions that are in a trigonal prismatic array. The molybdenum cations are sandwiched between two layers of close-packed S^{2-} anions, and the layers are held together by van der Waals forces. Within the layers, each sulfur anion is equidistant from three Mo^{4+} cations. Each Mo is coordinated to six S^{2-} in a trigonal prismatic array with edges of 3.15 Å, a height of 3.17 Å, and a molybdenum to sulfur spacing of 2.41 Å. Two major types of planes are exposed in crystallites due to the strong bonding in two dimensions and the weak van der Waals bonding between layers. There is the basal plane (0002) and the stable edge planes $(10\bar{1}0)$ and $(11\bar{2}0)$ shown in Figure 3. The basal plane is the most stable due to each sulfur having three bonds to molybdenum cations and each molybdenum is coordinated to six sulfurs. Therefore, both molybdenum and sulfur are coordinatively saturated in the basal plane. No molybdenum cations are exposed in the basal plane, only the sulfur anions are exposed. In the edge planes, the sulfur is coordinatively unsaturated having one or two

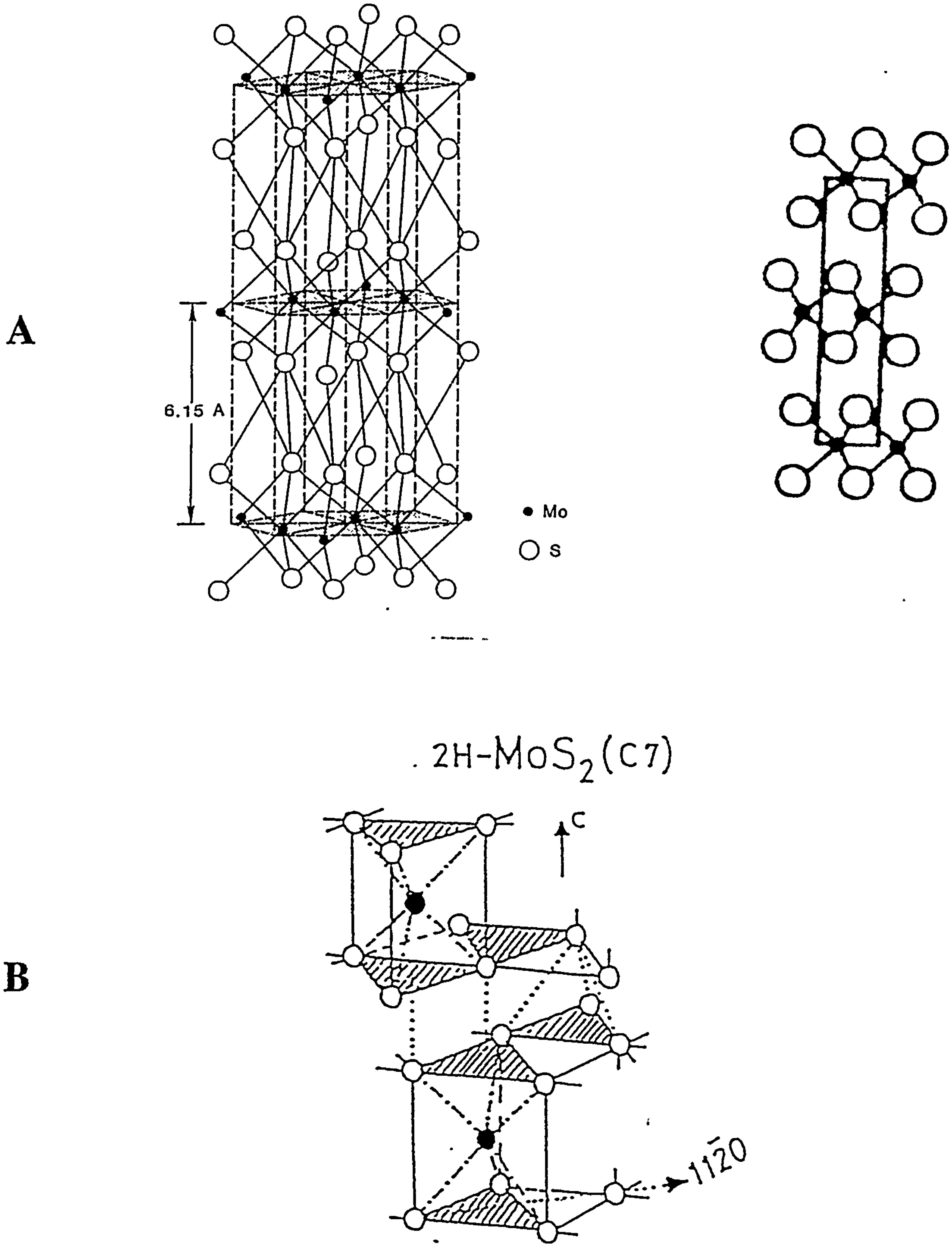

FIGURE 1. Representations of the crystal structure of hexagonal MoS_2 as taken from [A] Santiesteban, J. G., Ph.D. Dissertation, Lehigh University, May 1989 and [B] Wilson, J. A.; Yoffe, A. D., Advan. Phys., 1969, 18, 193.

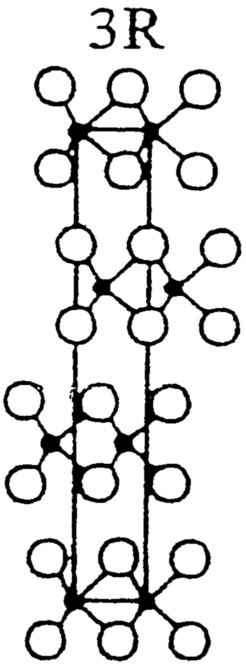

FIGURE 2. Representation of the crystal structure of rhombohedral MoS_2 as taken from Santiesteban, J. G., Ph.D. Dissertation, Lehigh University, May 1989. Note the additional layer compared with the hexagonal form of MoS_2.

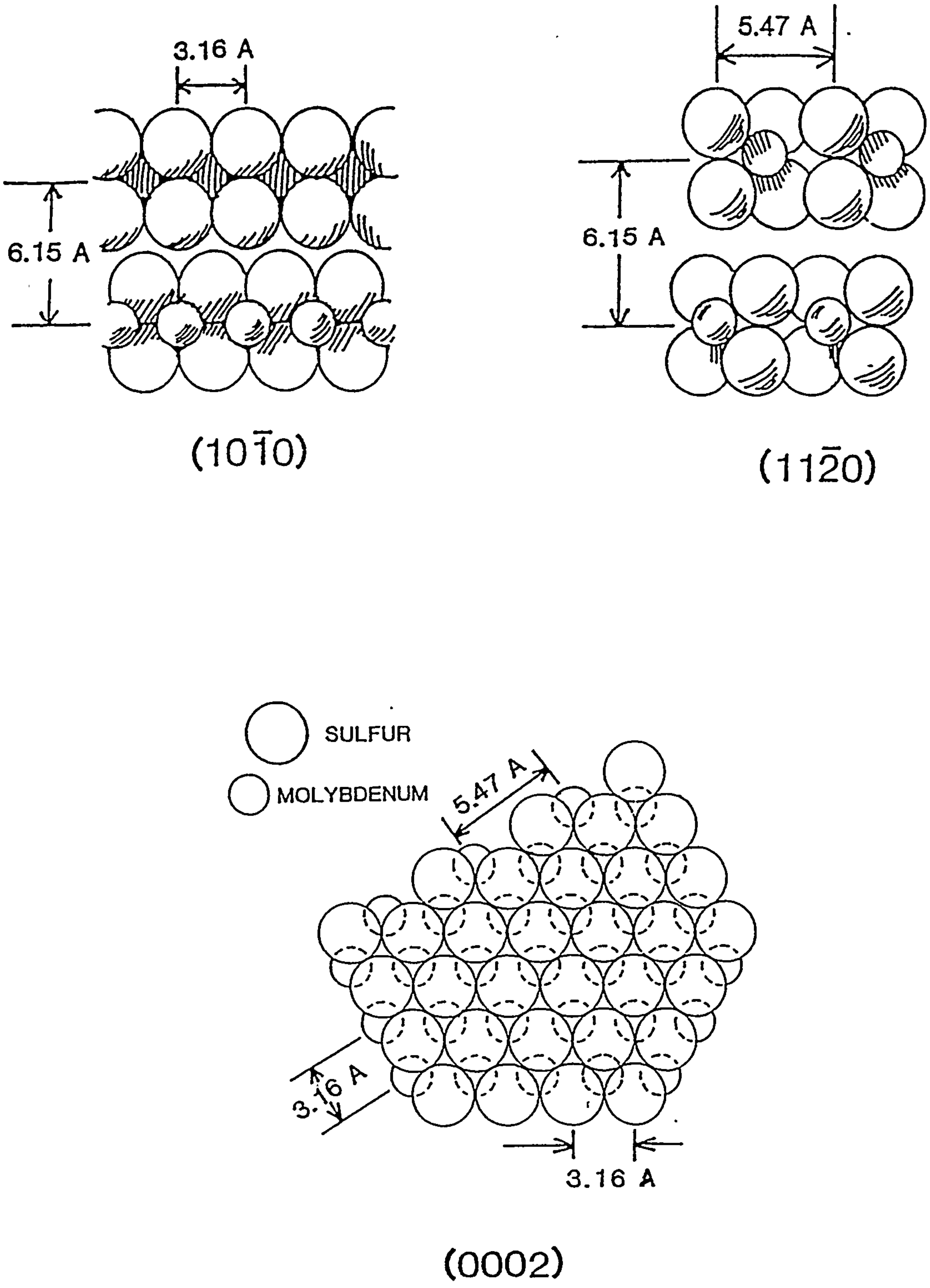

FIGURE 3. Representations of the (10$\bar{1}$0) and (11$\bar{2}$0) edge planes of crystalline MoS$_2$, as well as the (0002) basal plane.

bonds to Mo cations, and therefore the Mo is also coordinatively unsaturated in the edge planes [11]. Much work has been done to show that the edge planes of the MoS_2 are catalytically active and not the basal planes [16-19].

Role of Alkali Promoters in Molybdenum Disulfide

The use of alkali promoters is common throughout the field of heterogeneous catalysis, although in some case the alkali cations behave as poisons. The promoter is used to affect the selectivity and activity of the catalyst. It is not known whether this effect is chemical, electronic, or a combination of both. Mross studied the modes of action and the distribution of alkali promoters [20]. They came to the conclusion that there are at least eight modes of action of the alkali that must be considered, i.e.

1. Intrinsic catalytic effect of the alkali.
2. Creation of basic sites.
3. Neutralization of acid sites.
4. Modification of the electronic properties of the catalyst surface.
5. Auxiliary function during the preparation of the catalyst.
6. Modification of physical properties of an active component melt.
7. Reduction of the volatility of the active component through formation of compounds.
8. Prevention of phase transformations.

Mross [20] also came to the conclusion that the distribution of the alkali depends on the catalyst system used. In the case that the active component is present in the metallic form, the alkali spreads and forms a monomolecular layer. Only small amounts of alkali are needed of which there is an optimum concentration. Of the dopants in the alkali series, cesium has the most profound affect. In the second case where the active component is a melt, the alkali forms films on the surface and large droplets in pore cavities. The catalytic preparation is almost independent of alkali content when the alkali/active component ratio is held constant. It is possible to add large quantities of alkali in this case. For the third case where the alkali neutralized acid center, only extremely small amounts of alkali are needed and overdoping can cause a loss of catalytic activity.

Lee and Ponec studied the effect of alkali promoters on the Group VIII metals, and they came to the following three conclusions [21]:

1. The alkali promoter affects the propensity of the catalyst to dissociate carbon monoxide. It was assumed that the main pathway to hydrocarbons goes *via* dissociation of CO and then hydrogenation of surface carbon.
2. The alkali promoter with its positive charge stabilizes intermediates, such as formyl- and formate-like intermediates. In this case it was assumed that the main pathway to methanol is nondissociative with respect to carbon monoxide.
3. On the assumption that the main path to C_2+ oxygenates combines dissociative (CH_x and C_nH_n) and nondissociative (CO insertion) reactions of CO, the alkali promoter suppresses the dissociative reaction to the required level and stabilizes the intermediates of the oxygenates.

Lee et al. [22] sought to explain why alkali promoters sometimes promote chain growth, to give hydrocarbons, and at other times increase alcohol selectivity, which are mutually exclusive. Woo et al. in earlier studies [23-25] found that the distribution of the alkali on the surface and in the bulk affects the nature of promotion. In order to determine the nature of the promotional effects, samples of molybdenum disulfide were doped with various potassium salts. The distribution of the alkali was then studied using Auger electron spectroscopy (AES), X-ray dispersive spectroscopy (EDS), and elemental analysis. The results of the characterization were correlated with the catalyst performance at 300°C and 1.5 MPa.

Table 2 lists the potassium salts studied as well as the conjugate acid of the counter ion and its pK_a. Table 3 lists the performance of the different catalysts with nine hours on-stream at 573 K, 1.5 MPa, $H_2/CO = 1.0$, and $W/F = 8$ g cat*hr/mol. Table 4 lists the wt% of potassium by AES, EDS, and elemental analysis. Figure 4 shows the relationship between the pK_a of the acid and the space time yield of alcohols. It can be seen that the

TABLE 2

Acid form of the potassium salts used to dope the MoS_2 catalyst.

Acid of the Alkali Salt	pK_a of the Acid	Conjugate Base
HOH	15.7	OH^-
H_2CO_3	6.4	HCO_3^-
CH_3COOH	4.8	CH_3COO^-
HNO_3	-1.4	NO_3^-
H_2SO_4	-5.2	HSO_4^-
HCl	-7.0	Cl^-
HBr	-9.0	Br^-
HI	-10.0	I^-

TABLE 3

Steady-state (9 hr) activities and selectivities for the conversion of $H_2/CO = 1$ synthesis gas over unpromoted and K-promoted MoS_2 catalysts at 300°C and 1.5 MPa with flow rate corresponding to 8 g cat•hr/mol [From Reference 22].

Promoter	CO conv. (%)	CO_2 yield (%)	Carbon atom selectivity (%)		C_{2+}/C_1 ratio	
			H.C.	Alcohol	H.C.	Alcohol
None	35.3	17.3	99.2	0.8	0.72	0.0
K_2CO_3	8.4	3.5	38.8	61.2	0.25	0.70
KOH	13.7	8.3	52.0	48.0	0.56	1.34
KAc[a]	14.5	7.6	73.1	26.9	1.00	0.91
KNO_3	1.6	0.7	38.3	61.7	1.04	0.51
K_2SO_4	34.9	20.9	95.9	4.1	1.48	0.11
KCl	13.0	7.4	97.1	2.9	1.11	0.12
KBr	6.0	2.9	98.0	2.0	0.93	0.18
KI	3.2	1.6	98.4	1.6	0.83	0.60
K_2CO_3–Ox[b]	23.2	12.6	93.1	6.9	1.44	0.30
KOH–Ox[b]	38.9	28.9	97.7	2.3	1.49	1.56

[a] Potassium acetate.

[b] Oxidized by exposure to atmosphere for 11 weeks.

TABLE 4

The content of potassium (wt%) in/on the MoS_2 catalysts as determined by Auger electron spectroscopy (AES), X-ray dispersive spectroscopy (EDS), and chemical elemental analysis (CA).

Dopant on Catalyst	AES	EDS	CA
K_2CO_3, fresh	6.2	10.5	12.8
K_2CO_3, oxidized	1.3	3.4	12.7
KOH, fresh	7.1	5.2	7.0
K_2SO_4, fresh	≈0	1.9	9.8
KCl, fresh	≈0	0.7	9.7

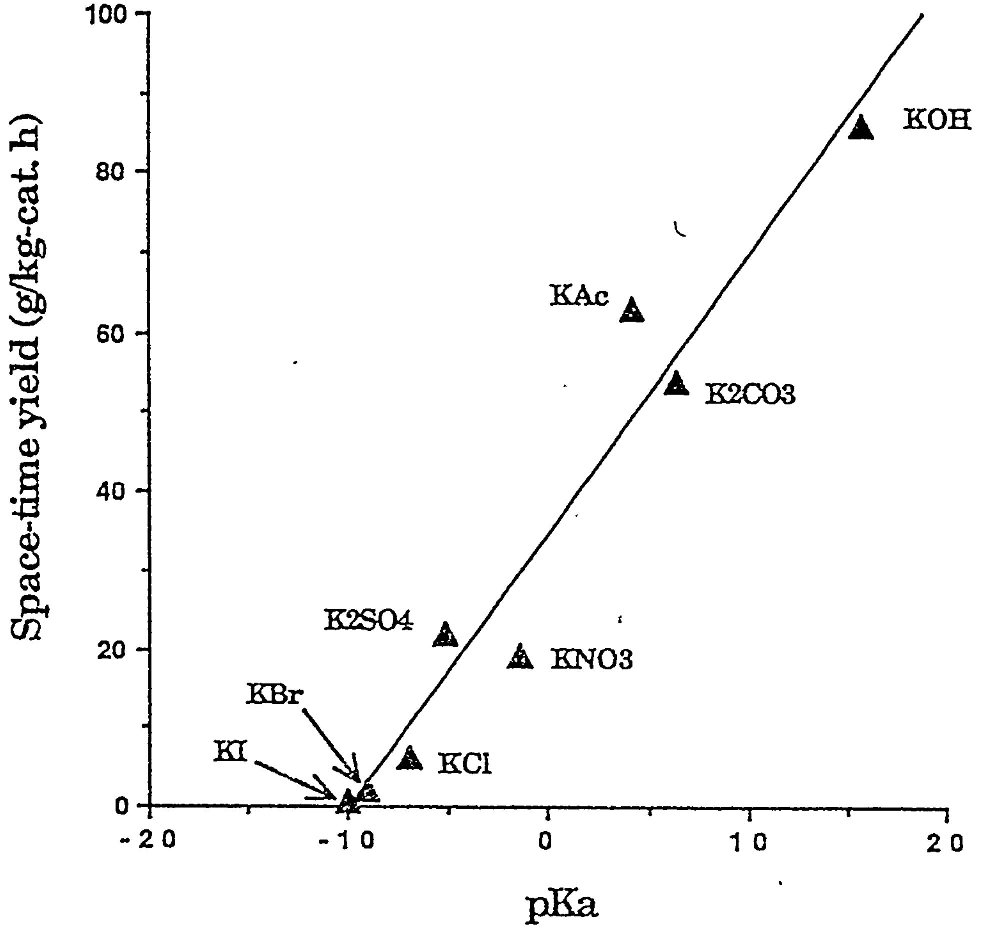

FIGURE 4. Relation between pK_a of the conjugate acids of the potassium dopants used and the space time yields of the alcohols produced over the MoS_2 catalysts (see Table 3 for reaction conditions and reference).

higher the pK_a (stronger base), the higher the space time yield of alcohols. The chain growth promoters have large negative pK_a values. As seen in the EM X-ray maps of the different catalysts, the catalysts that promote carbon chain growth tend to have a nonuniform dispersion, while the alcohol promoters have a uniform dispersion. The effects of alcohol promotion and uniform dispersion can be explained by the ease in which the alcohol promoters seem to remove their anions under the reaction conditions to give highly basic alkali species. The chain growth promoters, however, due to the strong electron affinity and thermal stability remain in their original chemical state during the reaction conditions and will aggregate with each other.

There was also an activation time necessary to reach steady state, as seen in Figures 5 and 6. In Figure 5, the longer the potassium sulfide (alcohol promoter) doped catalyst was on stream, the higher the selectivity to alcohols became before reaching a steady state. The potassium chloride (chain growth promoter) doped catalyst showed little increase in the selectivity to alcohols. Figure 6 shows that the CO conversion for the potassium sulfide doped catalyst decreased with time, while the CO conversion remained constant for the potassium chloride doped catalyst. This was explained as the time necessary for the alcohol promoter to uniformly spread themselves over the molybdenum disulfide surface and modify its surface reactivity. Santiesteban [11], also observed non-steady behavior under initial testing conditions for non-pretreated catalysts, and, therefore, cesium formate promoted MoS_2 catalysts were pretreated at 400°C for one hour at ambient pressure before catalytic testing in synthesis gas at elevated pressures and temperatures was begun.

Infrared spectroscopy studies have been carried out to probe the nature of surface intermediates. Common IR bands were seen for the alcohol selective catalysts near 1650 and 1400 cm^{-1} [22]. Figure 7 shows the comparison between catalysts that have been doped

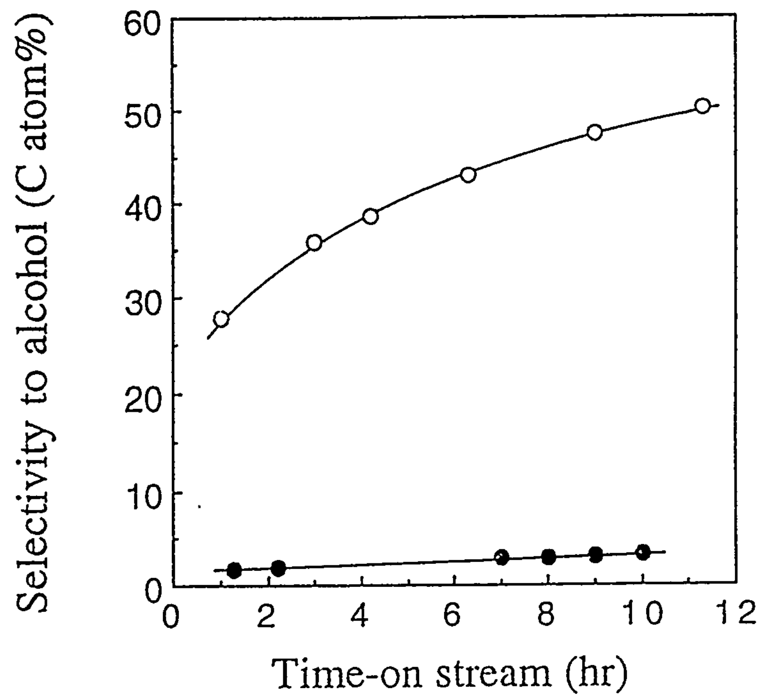

FIGURE 5. Alcohol selectivity *vs* time-on-stream for K_2S- (●, not shown in Table 3) and KCl- (○) promoted MoS_2 catalysts tested under the reaction conditions given in Table 3.

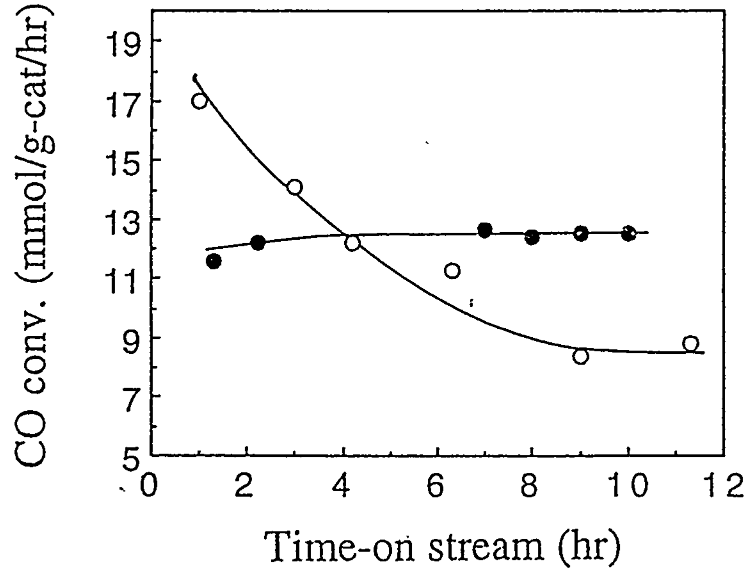

FIGURE 6. Total conversion of CO to products *vs* time-on-stream for K_2S- (●, not shown in Table 3) and KCl- (○) promoted MoS_2 catalysts tested under the reaction conditions given in Table 3.

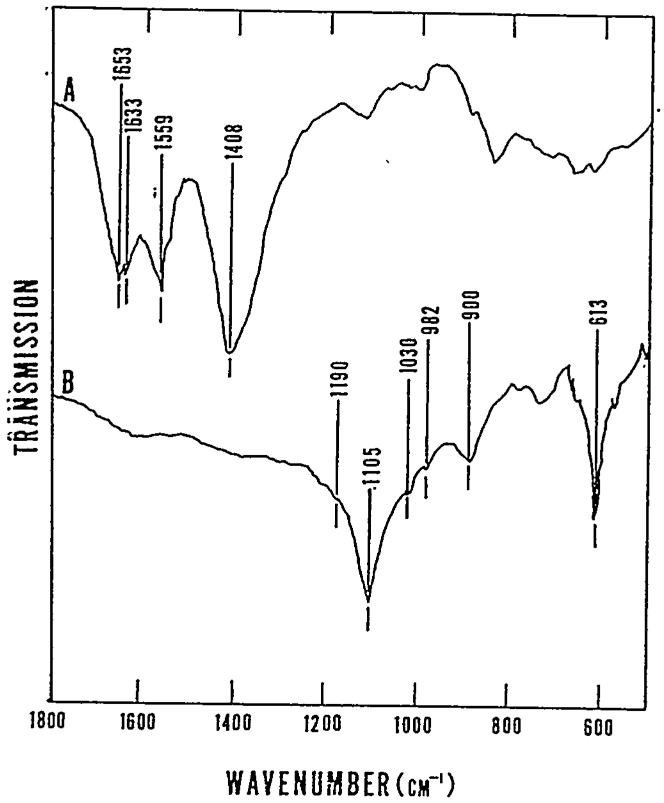

FIGURE 7. Infrared spectra of (A) a fresh K_2CO_3/MoS_2 catalyst and (B) a used K_2SO_4/MoS_2 catalyst tested at 300°C and 1.5 MPa pressure [22].

with alcohol promoters and with chain growth promoters. The chain growth promoters show none of the bands assigned to be common intermediates of all the alcohol promoters. These intermediates were also seen in other potassium promoted catalysts [26]. The bands near 1650 cm^{-1} were assigned to C-O-H bonds, and the bands near 1400 cm^{-1} were assigned to C-O-K bonds. The majority of the surface appeared to covered with these species. This coverage of the surface by these species is thought to reduce the hydrogenation activity of the catalyst by blocking the active sites for dissociative hydrogen adsorption. Also, the interaction of the surface with carbon monoxide will be weaker and direct hydrogenation without dissociation of the CO will dominate the pathway. Dissociative adsorption of CO on the catalyst surface is thought to lead to hydrocarbons.

The chain growth promotion, shown by KCl and K_2SO_4, is thought to be electronic in nature. In this case, the alkali donates an electron to the metal and increases the transition metal's electron density which enhances the dissociative adsorption of CO. The surface of the catalyst is now enriched with C_nH_m species and the probability of chain growth increases. The coverage of the promoter should be kept at such a level as to just modify the electronic states of the transition metal and not to block the active sites. This can be seen in the conversion of CO in Figure 5. The alcohol selective catalysts have a much lower CO conversion because the active sites for dissociative adsorption of CO are blocked. However, in the hydrocarbon selective catalyst, the potassium is subsurface and thereby not blocking the sites of dissociative CO adsorption. Therefore, more CO can be adsorbed on the hydrocarbon selective catalysts.

In earlier work by Woo et al. [23], a K_2CO_3/MoS_2 alcohol selective catalyst left exposed to the atmosphere lost its selectivity to alcohols and promoted chain growth. Through the use of XPS the molybdenum was shown to be oxidized from Mo(IV) to Mo(VI). There was also evidence of sulfates with T_d and C_{2v} symmetry formed on the surfaced to the MoS_2 in the IR spectra. Most of the potassium segregated into the bulk. Most of the K is located near the subsurface region of the MoS_2. This leads to a catalyst with a propensity for chain growth leading to hydrocarbons. It was shown that the oxidized K_2CO_3/MoS_2 catalyst had activity and selectivity similar to those observed with a K_2SO_4/MoS_2 catalyst.

It can be concluded from the work referenced above that the selectivity of the alkali-doped MoS_2 is strongly dependent on the alkali salt used and the handling of the catalyst before use, i.e. air should be excluded. Alcohol selective catalysts must have the alkali present on the surface of the catalyst, and this alkali salt must be readily dissociable under reaction conditions. The alkali on the surface is able to molecularly adsorb CO (covered in more detail later) and block hydrogenation sites. It was concluded that the distribution of the promoter is one of the primary factors governing its role in catalytic synthesis gas reactions.

The work of Santiesteban et al. [11, 27] with Cs-promoted MoS_2 catalysts is supported by many of the findings of the above described work. Santiesteban et al. used a variety of alkali metal salts and bases as dopants for MoS_2 catalysts. It was found that among the alkali metal dopants, cesium exhibited the best promotional effects, where the reaction conditions of 245-295°C, $H_2/CO = 0.96$, 8.3 MPa, and GHSV = 7750 ℓ/kg cat/hr were utilized. Under these conditions, a maximum doping level occurs at approximately 15-20 wt% $CsOOCH/MoS_2$, as seen in Figure 8. It was observed that doping the catalyst with alkali decreased the surface area. For instance, undoped MoS_2 had a BET surface area of 63 m^2/g, while 10 wt% $CsOOCH/MoS_2$ was determined to have a BET surface area of 17 m^2/g. This fits the idea that the alkali spreads and forms droplets at pores. This can be seen in electron microscopy pictures in Santiesteban's dissertation [11].

A series of cesium-doped catalysts were studied by electron microscopy, as listed in Table 5. Based on the results [11], the catalysts were divided into three classes: low loading (2.5 wt% CsOOCH), intermediate loading (5.3-20.0 wt% CsOOCH), and high loading (25.0-30.0 wt% CsOOCH). In the low loading case, the surface of the catalyst was a mixture of bare MoS_2 and highly dispersed cesium. This was determined using energy dispersive X-ray analysis (EDS). No cesium particles were seen using electron microscopy. In the intermediate loading case, the cesium was detected in a highly dispersed form, as well as in the form of particles. There were also areas of bare molybdenum disulfide. In the high loading case, the cesium was seen as particles, as well as in a film-like morphology.

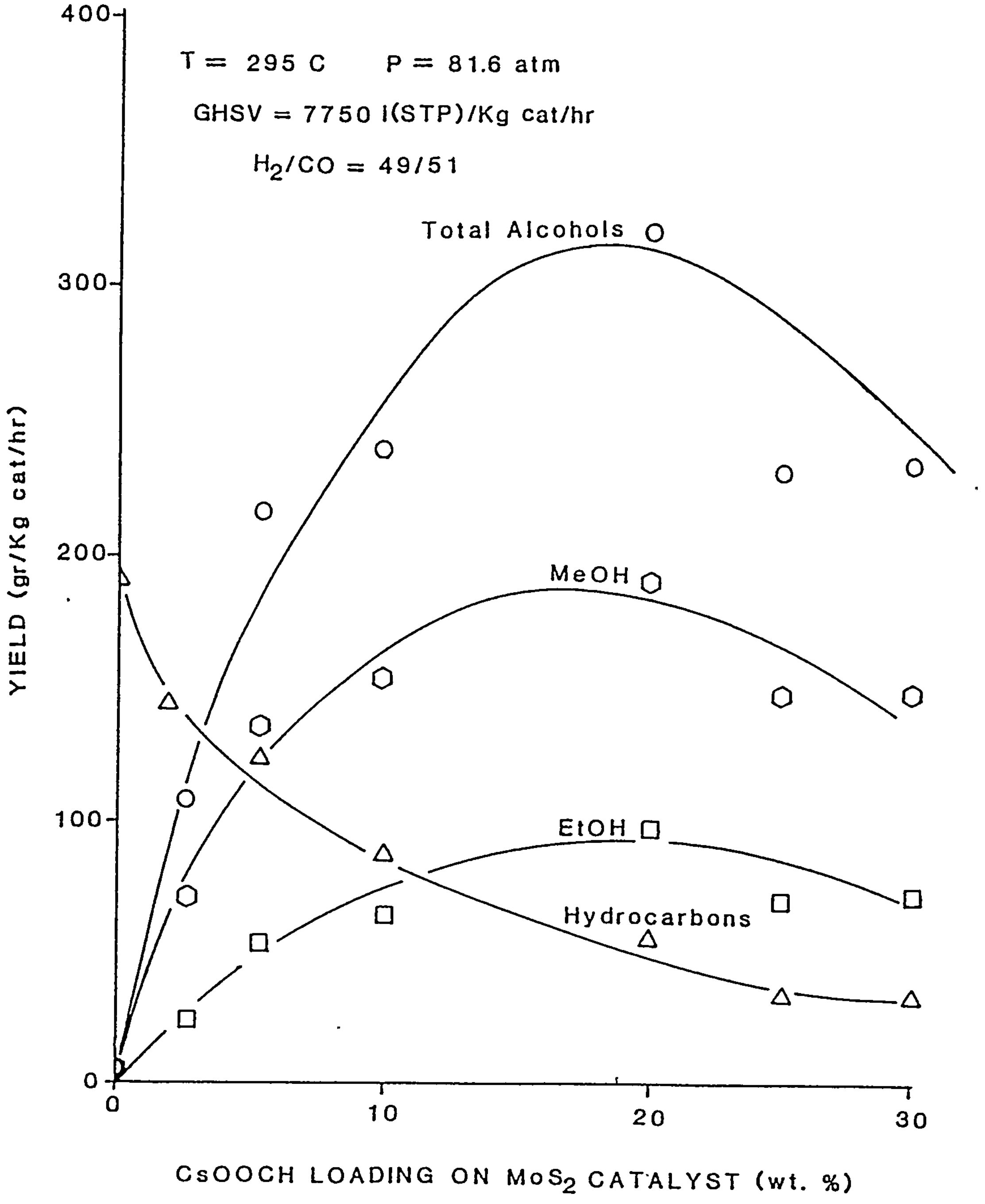

FIGURE 8. Effect of cesium content on the MoS_2 catalyst on the space time yield of products formed over the catalysts from $H_2/CO = 0.96$ synthesis gas at 295°C and 8.3 MPa with GSHV = 7750 ℓ/kg cat/hr [11,27].

TABLE 5

Composition of the Cs-doped MoS_2 catalysts.

CsOOCH (wt%)	CsOOCH (mol%)	mol Cs/mol MoS_2
2.5	2.25	0.023
5.3	4.77	0.05
10.0	9.09	0.10
20.0	18.36	0.22
25.0	23.07	0.30
30.0	27.83	0.38

It was determined in the previous work [11] that cesium in the highly dispersed state wets the surface of the edge planes and that hemispherical particles were formed on the basal plane. These particles are formed because cesium will not wet the surface of the basal plane. This was also seen by Kennou et al. [28], who studied cesium on the basal plane of MoS_2 and concluded that the cesium formed 3-dimensional clusters.

From the work reviewed, it can be deduced that the alkali promoter on molybdenum disulfide has several functions. First, the alkali promoter blocks active sites for the dissociative adsorption of hydrogen, as well as that of carbon monoxide. The alkali tends to disperse on the edge planes where hydrogen activation is proposed to occur (covered in more detail later). Also, the edge planes in the undoped catalysts will dissociatively activate CO to give carbidic intermediates, which can be hydrogenated to yield hydrocarbons, principally methane. The addition of the alkali serves to associatively activate CO to give different intermediates, which upon further reaction and hydrogenation selectively form oxygenates.