ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

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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 temperature, 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 $4d_{z^2}$, $4d_{x^2-y^2}$, 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 $\approx 7,800$ 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/MoS₂ catalyst, temperature, pressure, and flow rate dependences of the synthesis reactions were investigated in the presence and absence of H₂S in the H₂/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 H₂S in the synthesis gas did increase the C₂⁺ 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 H₂S 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 H₂S 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/MoS₂ catalyst, reproducible and high alcohol synthesis activity could be obtained. For example, at 295°C with H₂/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/MoS₂ catalyst was prepared by intercalation of metallic potassium from liquid NH₃ into MoS₂ 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 C₁-C₅ 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	---	----

^aReid vapor pressure (RVP) values are mainly from Piel, W. J., "Proc. 1st Biomass Conf. of Americas," Burlington, VT (1993).

^bEquivalent to 6.2 lb/gal.

^cEquivalent to 6.6 lb/gal.

^dFrom 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 TAE. Other ethers include methyl isobutyl ether (MIBE), isopropyl 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/Cr₂O₃.
2. Modified low pressure methanol synthesis catalysts, such as alkali-doped Cu/ZnO/Al₂O₃.
3. Modified Fischer-Tropsch or methanation catalysts, such as alkali-doped CuO/CoO/Al₂O₃ or alkali-doped MoS₂.

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 C₁-C₄ 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 MoS₂ produces alcohols from hydrogen-deficient H₂/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/MoS₂. 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 ($a = 3.16 \text{ \AA}$, $c = 12.19 \text{ \AA}$), which is written as 2H-MoS₂, is the morphology present in these catalytic systems and is shown in Figure 1. The rhombohedral form ($a = 3.16 \text{ \AA}$, $c = 18.38 \text{ \AA}$), written as 3R-MoS₂, 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 S²⁻ anions, and the layers are held together by van der Waals forces. Within the layers, each sulfur anion is equidistant from three Mo⁴⁺ cations. Each Mo is coordinated to six S²⁻ 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 MoS₂ 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 (1010) and (1120) edge planes of crystalline MoS₂, 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 $W/F = 8 \text{ g cat}\cdot\text{hr/mol}$. 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 MoS₂ catalyst.

Acid of the Alkali Salt	pK _a of the Acid	Conjugate Base
HOH	15.7	OH ⁻
H ₂ CO ₃	6.4	HCO ₃ ⁻
CH ₃ COOH	4.8	CH ₃ COO ⁻
HNO ₃	-1.4	NO ₃ ⁻
H ₂ SO 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 H₂/CO = 1 synthesis gas over unpromoted and K-promoted MoS₂ 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 ₂ CO 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 ₂ SO 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 ₂ CO 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

^aPotassium acetate.

^bOxidized by exposure to atmosphere for 11 weeks.

TABLE 4

The content of potassium (wt%) in/on the MoS₂ 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 ₂ CO ₃ , fresh	6.2	10.5	12.8
K ₂ CO ₃ , oxidized	1.3	3.4	12.7
KOH, fresh	7.1	5.2	7.0
K ₂ SO 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 MoS₂ 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 K₂S- (●, not shown in Table 3) and KCl- (○) promoted MoS₂ catalysts tested under the reaction conditions given in Table 3.

FIGURE 6. Total conversion of CO to products vs time-on-stream for K₂S- (●, not shown in Table 3) and KCl- (○) promoted MoS₂ catalysts tested under the reaction conditions given in Table 3.

FIGURE 7. Infrared spectra of (A) a fresh K₂CO₃/MoS₂ catalyst and (B) a used K₂SO₄/MoS₂ 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 be 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 K₂SO₄, 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 K₂CO₃/MoS₂ 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 surface of the MoS₂ in the IR spectra. Most of the potassium segregated into the bulk. Most of the K is located near the subsurface region of the MoS₂. This leads to a catalyst with a propensity for chain growth leading to hydrocarbons. It was shown that the oxidized K₂CO₃/MoS₂ catalyst had activity and selectivity similar to those observed with a K₂SO₄/MoS₂ catalyst.

It can be concluded from the work referenced above that the selectivity of the alkali-doped MoS₂ 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 MoS₂ 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 MoS₂ catalysts. It was found that among the alkali metal dopants, cesium exhibited the best promotional effects, where the reaction conditions of 245-295°C, H₂/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/MoS₂, as seen in Figure 8. It was observed that doping the catalyst with alkali decreased the surface area. For instance, undoped MoS₂ had a BET surface area of 63 m²/g, while 10 wt% CsOOCH/MoS₂ was determined to have a BET surface area of 17 m²/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 MoS₂ 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 $\text{H}_2/\text{CO} = 0.96$ synthesis gas at 295°C and 8.3 MPa with $\text{GSHV} = 7750\text{ l/kg cat/hr}$ [11,27].

TABLE 5
Composition of the Cs-doped MoS₂ 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 MoS₂ 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.

Activation and Incorporation of Carbon Monoxide

Of great importance in solving the mechanism of higher alcohol synthesis over alkali/MoS₂ are the questions of how carbon monoxide is activated and how the carbon monoxide is involved in chain propagation. In finding the actual sites of activation and propagation, the mechanism can be solved. There are two possible sites for activation and propagation. First is the alkali metal center, and the other is the molybdenum cations in the edge planes.

Mechanisms for Alcohol Synthesis From Synthesis Gas. The first step in alcohol synthesis is the activation of carbon monoxide. The two mechanisms usually considered involve either formyl or formate species. Reaction Scheme I shown on the next page is based on the formyl species stabilized on an active site (designated as *). The formyl species then can be further hydrogenated to give hydroxycarbene (I.A) or formaldehyde (I.B), which then can be farther hydrogenated to give methanol. Formyl species were identified by chemical trapping on nickel, rhodium, and palladium [29]. Formyl species have also been detected on Cu/ZnO using IR [30,31] and by trapping with amine [32]. In an isotope experiment over Rh/TiO₂ [33], a mixture of ¹³C¹⁶O and ¹²C¹⁸O and hydrogen was passed over the catalyst. ¹³CH₃¹⁶OH and ¹²CH₃¹⁸OH were produced, but not ¹³CH₃¹⁸OH or ¹²CH₃¹⁶OH. This was taken as evidence that the mechanism goes *via* formyl intermediate and excludes the formate pathway. The formate pathway would have caused isotope scrambling to give ¹³CH₃¹⁸OH and ¹²CH₃¹⁶OH.

In Scheme II, either CO or CO₂ reacts with activated H to form a surface formate. This formate is then hydrogenated to form methoxide and then methanol. Formate and methoxide species have been detected by IR on ZnO [34], iron, nickel, and cobalt [35], magnesia [36], and alumina [37] following adsorption of methanol onto these materials.

SCHEME I

SCHEME II

Using the argument of microscopic reversibility, these intermediates must participate in methanol synthesis. High pressure *in-situ* IR spectroscopy has been employed using CO₂ and H₂ over Cu/ZnO/Al₂O₃ [38,39] and CO and H₂ over Cs/Cu/ZnO and Cs/ZnO [40]. In the last example, CsOOCH was detected through IR identification. Isotope experiments [41] were also carried out in which D₂O was injected into H₂/CO mixture to give CH₂DO(H,D). It was concluded from this experiment that at least 65% of the methanol produced is formed *via* the formate mechanism.

It appears that on the noble metal catalysts, the main route to methanol is *via* the formyl pathway. However, on the Cu/ZnO-based catalysts, the main route to methanol can proceed *via* both formyl and formate intermediates.

There are three main mechanisms for the production of linear alcohols. First is the condensation of alcohols proposed by Frolich and Cryder [42] and Graves [43]. It was proposed that higher alcohols are formed *via* condensation of lower alcohols according to the following reactions:

The second mechanism is enol condensation proposed by Anderson et al. [44,45] and Emmett et al. [46,47]. As seen in Scheme III, the methanol precursor is the chain initiator. The synthesis of C₂⁺ alcohols occurs through hydroxycarbene intermediates followed by hydrogenation. Termination occurs by hydrogenolysis of the metal-carbon bond to form the corresponding alcohol. To account for the fact that hydrocarbons are also formed, the authors mentioned that adsorbed alcohols may be dehydrated to give hydrocarbons. The hydrocarbons would have the same chain growth probability.

Scheme III

Lastly is the CO insertion mechanism, described by Fischer and Tropsch [48]. They suggested that the formation of higher alcohols occurs from methanol and carbon monoxide through the following reactions:

These reactions involve the insertion of CO into C-O bonds to form a carbon-carbon bond, followed by hydrogenation of the intermediate. The direct participation of alkali in the mechanism was proposed by Natta et al. [49]. It was proposed that an alkali alkoxide is formed using KOH/ZnO catalyst, which is then reacted with CO followed by rearrangement to give alkali carboxylate. This is followed by hydrogenation to give the corresponding alcohol. Kiennemann and Hindermann see the insertion of CO into a carbon-oxygen bond as unlikely, since there is no model known for this homogeneous catalysis [50]. It appears that the first to propose CO insertion into metal-carbon bonds was Wender et al. [51]. Henrici-Olive and Olive [52] and Pichler and Schulz [53] proposed mechanisms involving CO insertion into metal-hydrogen bonds for initiation, as well as CO insertion into metal-carbon bonds for chain growth. This is shown in Scheme IV.

Computational Aspects of CO Insertion. There are two possible sites for activation of CO and for chain propagation on alkali-doped molybdenum disulfide which have been alluded in the above discussion of mechanisms. The two sites are the molybdenum atoms on the edge planes and the alkali dopant. The first thing to be discussed will be computational studies of CO insertions on second row transition metals. Next will be experimental evidence for CO insertions. And last will be possible activation mechanisms of carbon monoxide.

SCHEME IV

The reaction shown in Equation 6, where R = CH₃ or H, has been the focus of many theoretical studies using semiempirical and *ab initio* methods. Koga and Morokuma [54,55]

have recently reviewed the computational studies done on the carbonyl insertion reaction. The subject of many of these studies has been why is the insertion of CO into metal-carbon bonds more preferred than CO insertion into metal-hydrogen bonds. The conclusion reached by several authors [54-56], is that the carbonyl insertion into metal-carbon bonds is thermodynamically favorable over carbonyl insertion into metal-hydrogen bonds. It is believed that the metal-carbon bond is weaker than the metal-hydrogen bond, however, there are also other factors that influence the energetics of the process. One factor is that there is a larger gain in energy for the formation of the C-H bond than for the formation of a C-C bond.

Another important aspect that must be considered in chemical reactivity and stability is that of the interaction of the lone pair of electrons on oxygen with the metal. Early metals, which are oxophilic, tend to form η^2 -acyls and -formyls [57]. η^2 -Acyls have been seen experimentally on early transition metals such as zirconium and titanium complexes by Fachinetti et al. [58]. This has been studied theoretically by several researchers with varying levels of approximation [59-61]. For $\text{RMn}(\text{CO})_5$, Berke and Hoffmann, using extended Hückel computational analysis, found the η^1 -complex to be more stable [59]. However, Ziegler et al., using a local density approach, found the η^2 -complex to be more stable [60]. This result by Ziegler et al. was confirmed by Axe and Marynick using calculations at the Hartree-Fock level [61]. It appears that the more stable product is determined by the level of theory in the calculations.

In a study concerning the second row transition metals, Blomberg et al. [62] first investigated naked transition metal carbonyl complexes. Then, the effects of adding hydride or methyl ligands to the metal complexes were determined, after which calculations for the actual insertion reaction were carried out, and the barrier heights compared. The carbonyl binding energies are plotted in Figure 9. As can be seen, the largest (negative) binding energies are found at the right, with molybdenum having the smallest binding energy. The trend was explained to be the cause of two factors. First is the occupation of the metal d-shell, and secondly is the occupation of the 4s level. The 4s occupation is lower for elements on the right, leading to lesser repulsion of CO lone pair electrons. Also, for the elements to the right, the d-orbitals are doubly occupied leading to better back-donation. The elements to the left are only singly occupied. The elements to the left of molybdenum have the 4d-orbital unoccupied, and elements to the right can have the 5s state hybridize

FIGURE 9. Calculated metal-carbonyl binding energies for naked metal atoms and for metal hydrides, relative to the free initial species [62].

away the repulsive electrons. Molybdenum is the only element in the second row to have both repulsive 5s- and 4d-orbitals occupied. This is why molybdenum has the lowest binding energy with CO in the second row. The addition of a hydride or methyl ligand substantially increases the carbonyl binding energies. This is due to the removal of an electron by the added ligand from the repulsive sd region.

In Figure 10, the barrier heights for carbonyl insertion into metal-carbon and metal-hydrogen bonds is shown [62]. The barrier heights for the insertion into the metal-carbon bond are always much higher than for the insertion into metal-hydrogen bonds. This is explained to be due to the metal-alkyl bond being more directional than the metal-hydrogen bond. From the calculations, it can be seen that the observation of CO inserting into M-C bonds rather than M-H bonds cannot be explained as a kinetic effect. Therefore, it must be concluded that it is a thermodynamic effect, in agreement with other studies [55-57].

FIGURE 10. Transition state energies for carbonyl insertion into metal-hydrogen and metal-alkyl bonds [62].

As mentioned earlier, experimentally CO insertion into metal-carbon bonds is easier than the insertion into metal-hydrogen bonds. As seen in Figure 11, concerning the binding energies of the insertion product, the only metals for which the stabilities are considerably larger for acetyl than for the formyl complexes are ruthenium, rhodium, and palladium. For the rest of the metals, the stabilities are similar. The exception is zirconium, where the formyl is the more stable intermediate [62].

It can be concluded from these theoretical studies that insertion into metal-hydrogen bonds is unlikely when compared to the insertion of CO into metal-carbon bonds. This can be taken as evidence against the formyl mechanism, which involves the insertion of CO into a metal-hydrogen bond.

FIGURE 11. Reaction energies for carbonyl insertion into metal-hydrogen and metal-methyl bonds [62].

Experimental Evidence of CO Insertion. There are experimental examples of carbonyl insertion reactions occurring on molybdenum. For instance, CO will insert into a molybdenum methyl bond to give the acyl complex as shown in Equation 7 [63]. Equation 8 also shows another example of CO insertion into metal-carbon bonds. Incidentally, the rate of insertion is dependent of the substituent X on the benzyl group. Insertion is accelerated by electron-releasing and retarded by electron-withdrawing groups at the para position of the benzyl group [64].

One experiment that gives substantial evidence that the mechanism for chain growth over the alkali-doped molybdenum disulfide catalyst proceeds *via* CO insertion was performed by Santiesteban et al. [11,27,65]. ^{13}C -labelled methanol that was enriched by a factor of 21.69 over the natural ^{13}C abundance of 1.11 atom% was used as a gas phase dopant. After reaching steady state synthesis conditions over a $\text{CsOOCH/MoS}_2 = 20/80$ wt% catalyst at the following conditions, $\text{H}_2/\text{CO} = 0.96$, 8.2 MPa, GHSV = 7465 $\ell/\text{kg cat/hr}$, and temperature of 245-295°C, the labelled methanol was injected into the gas stream at a rate of 238.96 g/kg catalyst/hr. The liquid products were collected and analyzed by NMR and the gaseous products were analyzed by GC/MS. The enrichment factors for each carbon at various temperatures is shown in Table 6. It can be seen that the preferential enrichment occurred at the terminal carbons of the $\text{C}_2\text{-C}_4$ alcohols and at the methyl group of methyl esters and not at the carbonyl carbon. This result strongly suggests that the C_1 species initiates chain growth of C_2^+ alcohols and that the methyl group of methyl esters originates from methanol rather than from carbon monoxide. The labelled

methanol is incorporated as in Equations 9-10.

TABLE 6. Isotopic enriched of the carbon atoms in each product upon injection of $^{13}\text{CH}_3\text{OH}$ into the H_2/CO synthesis gas over a $\text{CsOOCH}/\text{MoS}_2 = 20/80$ wt% catalyst [11,27,65].

Temperature (°C)	^{13}C ENRICHMENT OF CARBON ATOMS			
	245	265	285	295
CH_3OH	17.7	14.2	11.9	7.4
CH_3	11.6	12.0	10.7	7.5
CH_2OH	1.3	1.4	1.5	1.1
CH_3	9.8	9.1	9.6	6.6
CH_2	-	-	2.4	1.8
CH_2OH	-	-	1.5	0.7
CH_3	-	-	9.0	5.9
CH_2	-	-	-	-
CH_2	-	-	-	-
CH_2OH	-	-	-	-
CH_3	21.8	26.2	18.9	25.7
O	-	-	-	-
HC=O	-	-	-	-
CH_3	12.6	15.9 ⁱ	9.8	9.7
O	-	-	-	-
C=O	-	-	-	-
CH_3	-	6.3	5.2	5.0

Further support for the CO insertion mechanism is provided by the observation that methane produced as a side-product was also labelled. The formation of methane is represented in Equation 11. This also supports the observation that in higher alcohol

synthesis, the products follow the Shultz-Flory-Anderson distribution if both alcohols and hydrocarbons are included. If the chain growth mechanism went by either enol condensation or alcohol condensation, there would have been isotope scrambling. Therefore, the evidence strongly suggests chain growth occurs *via* CO insertion.

With the evidence suggesting that the mechanism for chain growth is via CO insertion, the site for this activity has to be determined. There are two possible sites for CO insertion. One is the coordinatively unsaturated molybdenum on the edge planes. The other is the alkali dopant. As stated earlier, there are examples of CO insertions occurring on molybdenum organometallic complexes. There is also evidence that alkali can undergo a similar reaction. Tonner et al. [66] have demonstrated that alcohols can be carbonylated in the presence of alkali metals. Those experiments were carried out in an autoclave using 100 ml of the alcohol at 50°C and pressurized to 4.0 MPa with 99.8% pure carbon monoxide. The catalyst consisted of alkali alkoxides dissolved in the corresponding alcohol to give concentrations of alkali between 0.3 and 1.0 M. The reactions were found to be first order with respect to carbon monoxide. The rate of the carbonylation reaction was found to increase in the order: methanol < ethanol < n-propanol < n-butanol < i-butanol < i-propanol < t-butanol < secondary butanol. The rate of reaction was found to be dependent upon the solubility of the carbon monoxide in the corresponding alcohol. The trend for

solubility was found to be the opposite of the rate of carbonylation. The only products observed were the alcohol formates and a trace of alkali formate. The authors reported that the latter was problematic in that it reduced the amount of catalyst available. They suggested that the formation of the alkali formate came about from the reaction of the alkali hydroxide, caused by traces of water, and the alcohol as shown in Equation 12. However, the authors failed to give consideration to the formation of the alkali formates occurring through the reaction of CO and the alkali hydroxide, which is known to occur [67].

If the CO insertion does not directly take place on the alkali on the catalyst, it may participate in the insertion of CO on the molybdenum as has been proposed by a number of researchers [25,68-69]. Klier et al. [68] suggested that the alkali assists in C-C bond formation on alkali/Cu/ZnO catalysts *via* β -addition with oxygen retention reversal in oxygenate synthesis. Woo et al. [25] and Sachtler et al. [69] have proposed that the role of the alkali cation is very similar in nature to that of a Lewis acid for insertion reactions on transition metals. Scheme V shows the reaction scheme proposed [25]. The CO and hydrogen ligands occupy coordination sites on the molybdenum disulfide with the alkali, K in this case, bound to the oxygen of carbon monoxide (A). The CO inserts into the metal carbon bond forming an intermediate acyl complex stabilized by the potassium (B). Butts et al. [70] have proposed that Lewis acids bound to the more basic oxygen of the acyl carbonyl group increases the rate of insertion and helps stabilize the unsaturated intermediate.

As far as the activation of carbon monoxide, the sites for activation could be the same as for the insertion reactions. As mentioned earlier, binding of carbon monoxide to

SCHEME V

a transition metal activates the carbonyl to nucleophilic attack at the carbon by hydroxide for example to give the formate. Also, carbon monoxide is known to form alkali formates when it reacts with alkali hydroxides [67]. There has been spectroscopic evidence for the alkali formates [40]. So the experimental evidence showing CO insertion to occur into molybdenum-carbon bonds and the absence of CO insertion into molybdenum-hydrogen bonds, as well as spectroscopic results showing alkali formates, and computational studies showing the preference of CO insertion into metal-carbon bonds strongly suggests that CO is activated by the alkali dopant. However, there is a possibility that is at least to some extent activated on the molybdenum edge atoms. The isotope experiments by Santiesteban et al. [11,27] strongly suggest that the chain growth goes *via* CO insertion. It has been proposed that the alkali participates in the insertion of CO.

Activation of Hydrogen by Molybdenum Disulfide

Perhaps the most intriguing question concerning the mechanism of higher alcohol synthesis over alkali doped molybdenum disulfide is that of hydrogen activation. Very little is known about this topic. It is not known whether the activation, in other words the dissociation of molecular hydrogen, occurs through homolytic or heterolytic cleavage of the hydrogen-hydrogen bond. It is also not known where this activation takes place, for instance on the basal plane or the edge planes, or if it occurs on molybdenum or sulfur or both. Some of the solid state work done on undoped molybdenum disulfide will be presented as well as theoretical work.

Richards-Babb et al. [71,72] have performed extended Hückel calculations on molybdenum disulfide to determine which sites are more thermodynamically favorable for the adsorption of hydrogen. The calculation of the binding enthalpies showed that for the sulfur sites present in MoS₂ the fully-coordinated basal plane sites were over 1-coordinate and 2-coordinate edge sites. Of the basal plane sulfur sites, those systems with terminating edges were favored over infinite sheets. For the molybdenum sites, the 2-, 3-, 4-, and 5-coordinate sites were favored over the fully-coordinated sites. The order of stability was determined to be 2-coordinate edge Mo > 3-coordinate edge Mo > 3-coordinate basal plane S > 1- and 2-coordinate edge S > 4-coordinate edge Mo > 5-coordinate edge Mo > 6-coordinate basal plane Mo.

A theoretical ASED-MO study was performed by Anderson et al. [73]. The study was of hydrogen sorption on molybdenum-sulfur clusters. It was found that molecular hydrogen is heterolytically dissociated at 5-coordinate Mo edge sites. A second site was seen where the hydrogen atoms diffuse from the edge molybdenum atoms to sulfur anion basal plane sites.

The amount of hydrogen adsorbed by polycrystalline molybdenum disulfide has been the focus of much research. Badger et al. [74] reported that hydrogen adsorption by MoS_2 prepared from MoS_3 occurred at temperatures $>97^\circ\text{C}$. Later, Moyes [75] and Dianis [76] also reported this behavior for irreversible hydrogen adsorption on MoS_2 prepared by the decomposition of ammonium tetrathiomolybdate.

Wright et al. [77] studied the adsorption of hydrogen on MoS_2 prepared by the thermal reduction of MoS_3 by H_2 at 400°C . The sample was then degassed in vacuum at 300°C . A value of 0.089 moles of hydrogen per mole of MoS_2 was found. This is more than three times larger than can be accommodated on the BET surface area. This suggests that a portion of the adsorbed hydrogen is located in the bulk or else it is held in locations not accessible to nitrogen at 77K (-196°C). It was determined by measuring the surface area by the adsorption of CO_2 at -78°C that the hydrogen was accessible to nitrogen due to the results of the surface areas being the same.

MoS_2 prepared from molybdenum chloride and lithium sulfide and pretreated at 250°C in 20% $\text{H}_2\text{S}/\text{H}_2$ was subjected to differential scanning calorimetry [78,79]. There were two different hydrogen sorption sites found. The first site is populated at H_2 pressures of 0.66 atm and temperatures less than 150°C . At temperatures near 150°C , the sorption of H_2 increases rapidly. At temperatures above 150°C , the second site is populated and becomes saturated at pressures of approximately 5 MPa. It was found that the sorption of molecular hydrogen increased with increasing pressure. MoS_2 samples with the first site occupied were subjected to IINS experiments and showed excitations at 662 cm^{-1} and 872 cm^{-1} . The first excitation was assigned to S-H deformation mode of hydrogen bonded to a single sulfur atom on the surface. The second excitation was assigned to deformation modes of either Mo-O-H or Mo-H, with the Mo-O-H thought to be more likely. For

samples with both sorption sites occupied, and additional excitation near 400 cm^{-1} was seen that increased in intensity as the pressure of H_2 was increased. XRD was performed, and it was found that the occupation of the second site increased the lattice spacing.

The rate of hydrogen sorption by polycrystalline MoS_2 at 101 kPa and 52°C was studied by Blackburn and Sermon [80]. At infinite time, a stoichiometry of $\text{H}_{0.22}\text{MoS}_2$ was found. The rate of hydrogen sorption was found to be slow. After exposing the MoS_2 surface to H_2 for 60 minutes, a stoichiometry of $\text{H}_{0.1}\text{MoS}_2$ was found. The two sorption sites were studied with inelastic neutron scattering by Jones et al. [81]. The first site was found to be due to a Mo-S-H surface species indicating dissociation of H_2 on the molybdenum disulfide surface. Adsorbed molecular hydrogen was assigned to the second sorption site. As stated above in the computational section, Anderson et al. [73] attributed this site to the diffusion of hydrogen atoms from edge molybdenum atoms to sulfur in the basal plane.

Komatsu and Hall studied the sorption of hydrogen on microcrystalline MoS_2 and single crystal MoS_2 [82]. The microcrystalline MoS_2 was prepared from ammonium tetrathiomolybdate by rapid heating of the precursor from 22°C to 350°C in a flow of 14% $\text{H}_2\text{S}/\text{H}_2$. The MoS_2 was then passivated in 10% O_2/He at -196°C (77K) for 30 min and then another 30 min at 22°C , resulfided in 14% $\text{H}_2\text{S}/\text{H}_2$ at 400°C for 1 hr, reduced in dry hydrogen at 500°C for 1 hr, and then flushed with purified He or N_2 at 500°C for 1.5 hr. This sample showed no adsorbed hydrogen. Hydrogen was then rapidly adsorbed on this sample at a pressure of 72 kPa and -196°C . The adsorbed hydrogen was thought to be molecular hydrogen H_2 since it desorbed at -78°C . Adsorption studies were also carried out at 27°C and in the temperature range of 350 to 773°C , and the adsorption at each temperature was monitored by temperature programmed desorption (TPD), microbalance,

and isotope dilution [82].

Analysis of the data was carried out to determine quantitatively how much hydrogen was adsorbed onto the MoS₂ sample, and the number of moles of hydrogen adsorbed relative to Mo atom at each temperature is shown in Table 7. It can be seen that the number of moles of hydrogen adsorbed decreases with increasing temperature. The stoichiometry of the sample also changed such that the number of moles of S per Mo atom decreased from an initial value of 1.983 to 1.953 after adsorption at 500°C. For this sample, the TPD data showed the start of hydrogen desorption at 97°C, and the overall desorption of H₂ occurred as a broad peak centered at 247°C. At 180°C, increasing the pressure of H₂ increased the uptake of hydrogen by the sample. The adsorbed amount of hydrogen went up with increasing surface area of the sample. Upon extrapolation of the hydrogen uptake to zero surface area, it was indicated that there would be a significant amount of uptake. This is in support of earlier reports that indicate hydrogen may be present within the Van

TABLE 7
Experimentally determined values of x and α for H _{α} MoS _{α}
at 0.1 MPa and 180°C [82].

Temperature of H ₂ Pretreatment (°C)	Surface Area (m ² /g)	α	x Using Micro-balance	x Using TPD	x Using Isotope Dilution
350	55	1.983	0.044	0.045	---
400	43	1.960	0.038	0.040	0.041
450	32	1.956	0.030	0.029	0.028
500	17	1.953	0.019	0.018	0.016
350 (fresh) ^a	55	1.983	0	0	<0.001

^aBlank (before H₂ adsorption)

der Waals gap. These samples were also studied using ^1H NMR. All of the samples gave one broad peak at approximately 2 ppm. This value was found to consistent with H bound to S, as with SH groups or with nonacidic OH groups.

From the solid state research, it appears there are two sites for the adsorption of hydrogen. The first appears to be on the sulfur since evidence for SH groups has been found [78-80,82]. The second appears to consist of hydrogen adsorbed between the MoS_2 layers. From the research of Komatsu and Hall [82], evidence for the adsorption of hydrogen occurring on edge sites has been obtained.

EXPERIMENTAL PROCEDURES

Preparation of Sulfide Catalysts

Preparation of MoS₂. Preparations of this catalyst included synthesizing two batches of MoS₃ under identical conditions. In a hood, 108 ml portions of 20% aqueous (NH₄)₂S were added to 15.1520 g (Batch 1) or 15.0887 g (Batch 2) of (NH₄)₂Mo₇O₂₄•H₂O in an 800 ml beaker. The solution was stirred using a magnetic stirring bar and heated to 60°C. The solution turned a very deep red color as the (NH₄)₂Mo₇O₂₄•4H₂O dissolved.

An acid solution consisting of 100 ml of glacial acetic acid diluted to 400 ml using distilled water was prepared. This acetic acid solution was then added to the (NH₄)₂Mo₇O₂₄•4H₂O and (NH₄)₂S solution, and the heat was turned off but stirring was maintained for 3.5 hr. The resultant very dark brown precipitate was filtered in a Buchner funnel and washed well with distilled water. The product was dried in an oven at 110°C overnight.

A third large batch of MoS₃ was prepared (Batch 3) using 15 g (NH₄)₂Mo₇O₂₄•4H₂O and 106 ml of 22% aqueous (NH₄)₂S. The MoS₃ was washed with distilled water and dried overnight in air at 120°C.

Samples of MoS₂ were prepared by calcination of MoS₃ under the flow of various gases. In each case, several 2-3 g portions of MoS₃ were calcined and then the portions were combined to form a larger batch of MoS₂. Gases utilized during the calcination treatment were:

1. **Helium**: Catalyst Treatment A. For this treatment, 2-3 g portions of MoS₃ were mixed with 3 mm Pyrex beads. In a quartz tube (I.D. = 8 mm) about 61 cm long, glass wool was placed 10 cm from one end. The Pyrex beads/MoS₃ mixture was then added to

the tube, and another layer of glass wool was put on top of the mixture. More clean Pyrex beads were added with another layer of glass wool near the end of the tube. The quartz tube was then placed in a horizontal split-tube furnace and connected to a helium tank. The flow rate of the helium was set at 60 ml/min and checked periodically with a bubble meter. The temperature was turned up to 200°C quickly using a differential heating devise and held for 10 min. Then the temperature was increased to 450°C for 1.5 hr. The clean Pyrex beads near the outlet end of the tube were cool and collected the released sulfur by condensation as the MoS_3 was decomposed into black MoS_2 . The MoS_2 product was then separated from the Pyrex glass beads using a sieve in ambient air and placed in sample bottles.

2. Nitrogen: Catalyst Treatment B. The same procedure was used as outlined above, except the purge gas that was used consisted of purified N_2 .

3. $\text{H}_2\text{S}/\text{H}_2$ Mixture: Catalyst Treatment C. In this case, a gas mixture of 204 ppm H_2S in hydrogen was used as the pretreatment gas. The same procedure was used as outlined above.

10 wt% $\text{CsOOCH}/\text{MoS}_2$ Catalyst-Sample 1. MoS_3 Batch 3, diluted with Pyrex beads, was used to prepare to prepare MoS_2 . The resultant MoS_2 , with a surface area of 60 m^2/g , was doped by impregnation with CsOOCH under vacuum. A 0.2339 M aqueous solution of cesium formate was prepared. This was made by weighing out 4.0488 g of 99.9% cesium formate and diluting it to 100 ml with distilled water. For a 10% doping level, 3.32 ml of the 0.2339 M solution was needed, which was diluted further with distilled water to approximately 40 ml.

The diluted cesium formate solution was introduced using a vacuum system as is pictured in Figure 12 [11]. The molybdenum disulfide (1.2100 g) was placed in the flask, and the apparatus was connected to the vacuum manifold. The sample and the apparatus

FIGURE 12. Diagram of the vacuum apparatus used in the preparation of alkali-doped MoS_2 catalysts.

were evacuated at 105°C for 2 hr and then cooled to room temperature. Using a syringe, 10 ml of the diluted CsOOCH solution was added to the MoS_2 . This was heated to 60°C under vacuum, and the solid was allowed to go to dryness. This was repeated until all of the CsOOCH solution (40 ml) was added. The apparatus was then detached from the manifold, and the 10% Cs/MoS_2 catalyst was scraped from the flask. After detachment from the vacuum system, no effort was made to exclude air from the sample.

10 wt% $\text{CsOOCH}/\text{MoS}_2$ Catalyst-Sample 2. Another 10 wt% $\text{CsOOCH}/\text{MoS}_2$ catalyst was prepared from MoS_3 Batch 3. In this preparation, the MoS_3 was not diluted with Pyrex beads, but ≈ 3 g was centered in a 51 cm long quartz tube. Decomposition was carried out in flowing N_2 (60 ml/min), by raising the temperature to 250°C , which was maintained for 30 min. The temperature was then increased to 450°C as fast as possible ($\approx 20^\circ\text{C}/\text{min}$) and equilibrating for 2 hr. Maintaining the flowing N_2 , but the resultant MoS_2

was cooled to ambient temperature.

Immediately after cooling, 2.1189 g of the MoS_2 was weighed and placed in the vacuum apparatus shown in Figure 12. The sample was heated to 100°C for 2 hr and then cooled to ambient temperature. Three equivolume portions totalling 10.5 ml of a 0.1224 M CsOOCH solution were added to the catalyst in the vacuum *via* syringe. The high purity CsOOCH was obtained from the Cabot Corp. Each portion of the solution was just enough to cover the catalyst. The sample was allowed to dry under vacuum at 60°C before the next portion of CsOOCH solution was added. After the third portion, the catalyst was dried and maintained under N_2 overnight. Under a N_2 atmosphere, 1.7313 g of the catalyst was weighed, mixed with 6 ml of 3mm Pyrex beads, and centered in the catalytic reactor.

$\text{CsOOCH}/\text{MoS}_2 = 13/87 \text{ wt\% Catalyst}$. For the cesium-promoted catalyst prepared for catalytic testing, the MoS_3 was calcined under nitrogen (from Batch 1, designated as Catalyst 1B). However, after calcination in flowing nitrogen, the MoS_2 was not allowed to come in contact with air, but rather the closed tube was moved into an adjacent nitrogen-filled glovebox. The MoS_2 was placed in a small beaker, and to this was added 0.2339 M CsOOCH aqueous solution. The sample was allowed to evaporate to dryness under nitrogen, and the resultant catalyst corresponded to $\approx 9 \text{ wt\% Cs}/\text{MoS}_2$. Chemical analyses of the undoped MoS_2 catalyst and of the CsOOCH -doped catalyst are given in Table 8. Thus, the analyses correspond to $\text{MoS}_{2.00}$ (Batch 1, Sample A) and 12.89 wt% $\text{CsOOCH}/\text{MoS}_{1.92}$.

$\text{CsOOCH}/\text{MoS}_2 = 20/80 \text{ wt\% Catalyst}$. The MoS_2 catalyst was prepared from MoS_3 (Batch 3) using flowing nitrogen during the decomposition treatment (Treatment B). The disulfide was then doped with cesium using a methanolic solution of 0.1993 M cesium formate. The cesium formate solution was added in 10 ml aliquots and evaporated to

dryness in air. The volume of solution utilized yielded a nominally 20 wt% cesium-doped molybdenum disulfide.

TABLE 8
Chemical analyses^a (wt%) of the Catalyst B MoS₂ and
of the freshly prepared CsOOCH/MoS₂ catalyst.

Sample	Cs	Mo	S
MoS ₂ (1B)	---	57.34	38.33
Cs/MoS ₂	9.63	50.26	32.28

^aAnalyses carried out by Galbraith Laboratories

K/MoS₂ = 12.5/87.5 wt% Catalyst. The preparation procedure employed with this catalyst aimed at preparing MoS₂ containing intercalated potassium. Approximately 4 g of MoS₃ was placed in the center of a quartz tube reactor, using Pyrex beads for centering, that was 51 cm long and had an inner diameter of 8 mm. The tube was placed in a horizontal tubular furnace and a flow of N₂ was maintained at 60 ml/min. Using a differential heating devise, the temperature was raised to 250°C and held for 25 min. The sample was then heated to 450°C as fast as possible and maintained at this temperature for 2 hr. The sample was then cooled to ambient temperature while maintaining the N₂ flow.

A 1.7191 g portion of the MoS₂ was placed in a 50 ml round bottom flask (Vessel A in Figure 13), heated to 60°C, and subjected to a vacuum supplied by a rotary pump for 2 hr. The glass system shown in Figure 13 was then filled with argon, and the round bottom flask was plugged and placed in an argon-filled glove bag.

The ammonia used as the intercalation solvent was purified so that no iron impurities were present. A freeze/thaw technique was utilized in which a 50 ml round bottom flask

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FIGURE 13. Apparatus used to prepare MoS_2 catalysts intercalated with potassium.

(a clean Vessel A in Figure 13) was nearly filled with liquid ammonia, which was then frozen with liquid N_2 . The complete system was evacuated for 5 min with all stopcocks open, and then the stopcock to the vacuum trap was closed and the empty Vessel B (Figure 13) was cooled to below room temperature. The frozen ammonia in Vessel A was allowed to thaw and vapor transfer of the ammonia from Vessel A to Vessel B occurred. The transferred liquid ammonia was then poured from Vessel B into a dewar that was exposed to air but flushed with argon while the transfer was taking place until ≈ 100 ml of liquid ammonia was in the dewar. The dewar was placed in an argon-filled glove bag, which was then flushed several times with argon before 0.2150 g of potassium metal was added to the liquid ammonia. To the resultant blue liquid ammonia/potassium mixture was added 1.7191 g of MoS_2 . While maintaining a constant flow of argon through the glove bag overnight, the mixture was allowed to stand overnight until all of the liquid ammonia had evaporated. The

black solid was then removed from the dewar and placed in a clean 50 ml round bottom flask, attached to the vacuum system shown in Figure 13 as Vessel A, heated to 50°C, and evacuated for 2 hr. The flask was plugged, placed back into the argon-filled glove bag, and most of the 12.5 wt% K/MoS₂ sample (1.3981 g) was mixed with 6 ml of 3 mm Pyrex beads for loading into the stainless steel tubular reactor under argon for subsequent catalytic testing.

Determination of the Surface Areas of the MoS₂-Based Catalysts

The surface areas were measured on a Gemini 2360 instrument using the BET multipoint method. Nitrogen was used as the adsorbate, and no free space correction was applied. Typically, 7-10 data points were taken from $p/p_o = 0.05$ to $p/p_o = 0.30$.

The samples were weighed in air in the analysis tube, and they were then degassed by heating to 300°C in a flow of nitrogen for two hr. The samples were cooled to room temperature under nitrogen, reweighed, and then the surface areas were measured at liquid nitrogen temperature.

Catalytic Testing of MoS₂-Based Catalysts

Catalytic testing was typically carried out with a stainless steel reactor tube with a length of ≈ 76 cm, which had an internal thermocouple. Centering the catalyst in the reactor consisted of adding 29-30 cm of 3.0 or 5.0 mm Pyrex beads, and then a layer of glass wool was put on top of the Pyrex beads. The catalyst to be tested, e.g. 2 g, was mixed with 7-8 ml of 3 mm Pyrex beads, and the Pyrex bead/catalyst mixture, the volume of which corresponded to a bed height of 10 cm, was then added to the reactor. Glass wool was added, and the tube was filled to the top with more clean Pyrex beads. Another layer of glass wool was added and the top was closed except for a small hole at the top and bottom

Swagelok fittings, which were covered with parafilm. The tube was taken out of the glove bag, and wrapped in brass sheaths, which were used to distribute heat evenly around the reactor tube during catalytic testing. There was another thermocouple connected to the center outside wall so that one could monitor the temperature of the outside reactor wall, as well as the internal bed temperature. The reactor tube was centered in the vertical furnace and connected to the H_2/CO reactant synthesis gas system.

The catalyst testing reactor system has high pressure and high temperature capabilities, and the entire apparatus is made of 316 stainless steel. A schematic diagram of the catalyst testing system is shown in Figure 14. The inlet gas manifold typically had four tanks of gas connected to it. These consisted of H_2 , CO , N_2 , and 2 vol% $\text{H}_2/98$ vol% N_2 , each with its own flow regulator and in-line pressure gauges. All of the gas lines converge into a reactor inlet tube before the pressure gauge that measures the pressure at the top of the reactor. There is also a high pressure Gilson pump connected to the gas inlet above the reactor for the injection of liquids if desired. The temperature of the electric furnace is controlled by a proportional controller interfaced with the thermocouple on the reactor wall. At the bottom of the reactor, an outlet tube wrapped in heating tape carries the products to a back pressure regulator, which controls the pressure in the reactor. After the back pressure regulator, the outlet tube is directly connected to heated in-line sampling valves on a Hewlett-Packard 5730A gas chromatograph, all of which are controlled by PC data station interfaced with a Hewlett-Packard 3396 Series II integrator. The products and excess gases are then sent to a bubble meter that monitors the gas flow rate.

After connecting the reactor to the catalyst testing unit, the MoS_2 -based catalyst was reductively pretreated at ambient pressure before testing. The temperature was brought up to 400°C under a flow of 2 vol% $\text{H}_2/98$ vol% N_2 with a rate of 60 ml/min for 1 hr in order

FIGURE 14. Schematic diagram of the alcohol synthesis reactor system used to test the undoped and alkali-doped MoS₂ catalysts.

to get rid of any surface sulfates that might have formed. Then the reactor was allowed to cool overnight. With only H_2/CO synthesis gas flowing, typically preset to a H_2/CO molar ratio of 1/1, through the system, the reactor was pressurized and catalytic testing was begun. In general, the reaction temperature was varied stepwise while keeping all other reaction conditions constant.

Theoretical Calculations

Calculation of Valence Band Spectra. A solid state adaptation of the extended Hückel theory is a very simple method that will calculate the density of states, as well as the contributions of the valence atomic orbitals to the density of states. The package used for these types of calculations is entitled "Extended Hückel Molecular, Crystal and Properties Package" [83], which was obtained from the Quantum Chemistry Program Exchange (QCPE). Some features of this program are the ability to calculate the density of states (DOS), energy dispersion curves, orbital character of energy bands, total energy, and electron population for a variety of systems, all to the same level of approximation. The theory is essentially an empirical one-electron theory in which correlation effects are not taken into account. Additional information in regard to the use of this program for studying the electronic properties of particular crystal planes of transition metal sulfides has been given previously [72].

Input parameters necessary for calculating a specific TS_2 density of states are the following: x,y,z coordinates of the atoms in one unit cell; Slater type orbital exponents, ζ_i , and coefficients, c_i ; atomic ionization potentials, H_{ii} ; and the k-points (wavevector) and weighting factor at which the calculation is to be carried out. Thus, the input parameters, specifically the atomic ionization potentials and Slater-type coefficients, can be parametrized

with respect to experimental data. For instance, once the S 3s, 3p H_{11} , ζ_1 and c_1 parameters are found for one TS_2 compound, e.g. MoS_2 , these parameters can be used in a study of the electronic properties of a series of TS_2 compounds.

RESULTS

Consideration of the Thermodynamic Stability of Transition Metal Sulfides

The stability of a catalyst under the reactor conditions employed is very important in any investigation into the development of a new catalyst system. Previous catalytic studies on alkali doped MoS₂ have shown that this catalyst is stable for long periods of time at pressures of 8.2 MPa and temperatures ranging from 250°C to 350°C [65]. However, knowledge about the stability of related transition metal disulfide systems is unavailable experimentally. For this reason an investigation of the thermodynamic properties of the third, fourth, and fifth period transition metal (T) disulfides, TS₂, has been carried out. In the reactor, H₂ gas is present as one of the reactants in the synthesis gas used for higher alcohol synthesis over these catalysts. The water gas shift (WGS) reaction and production of hydrocarbons from synthesis gas are both reactions that can produce H₂O (or consume H₂O in the case of the forward WGS reaction) in the reactor. For these reasons, the stability of the catalyst in a hydrogen environment towards its corresponding metal and most stable sulfide and oxide forms is valuable information. This information can be calculated from available thermodynamic data [84-86].

The overall reaction for the reduction of transition metal disulfides by H₂ is shown in Equation 13. Calculated Gibbs free energies at 298K and 0.1 MPa pressure are shown

in Figure 15. The most stable TS₂ compounds will be the ones with the most positive ΔG values. As can be seen from the trends in Figure 15 the stability of the TS₂ toward its corresponding metal, T, decreases as one proceeds across each period. The most stable compound having a layered structure is NbS₂, while the most stable pyritic compound is

FIGURE 15

Stability of TS_2 Toward Reduction ($T=298K$, $1atm$)

RuS₂. In general, the thermodynamically most stable compounds are found in the fourth period.

When the stability of the TS₂ compounds are compared to the corresponding most stable oxide forms, the trend is markedly different. The general overall reaction for oxidation of the TS₂ compounds is shown in Equation 14. Calculated Gibbs free energies at

298K and 0.1 MPa pressure are shown in Figure 16. Again, the most stable TS₂ compounds will be the ones with the most positive ΔG values. As can be seen from Figure 16, the layered compounds NbS₂ and TaS₂ are very unstable toward oxidation to Nb₂O₅ and Ta₂O₅, respectively. Also, the third period TS₂ compounds are only moderately stable toward oxidation to Mn₃O₄ and Fe₃O₄(Fe₂O₃). As can be seen from the trends in Figure 16, the stability of the TS₂ compounds toward oxidation increases as one proceeds across each period. This trend is opposite to that found for reduction. Again, the fourth period TS₂ compounds are the most stable. Since the trends in stability are opposite for the two tests of reducibility and oxidizability, both stability criteria must be considered when choosing a catalyst. From this analysis, compounds with intermediate values of Gibbs free energy for both reduction and oxidation should be the most stable under the catalytic conditions employed. For example, the layered compounds MoS₂, WS₂, and ReS₂ and the pyritic compound RuS₂ should be the most stable compounds.

Precaution must be observed when analyzing the thermodynamic calculations presented in the preceding paragraphs. The calculations presented were obtained by using the thermodynamic values of bulk TS₂ compounds. However, the active portion of a catalyst

FIGURE 16

Stability of TS_2 Toward Oxidation ($T=298K$, 1atm)
 $MS_2(s) + (y/x)H_2O \rightleftharpoons (1/x)M_xO_y(s) + 2H_2S(g) + [y/(x-2)]H_2(g)$

is actually the surface and not the bulk. The surface may consist of atoms with dangling bonds and unshared vacancies, and thus surface thermodynamics may be different from those of the bulk. However, to a first approximation the trends exhibited for the bulk can be assumed to be similar for the surface. An increase in pressure will not affect the reduction and oxidation reactions since the number of moles of reactant and product gases is equal.

Investigation of Electronic Structure

Theoretical calculations can provide insight into the electronic properties of materials that determine their experimental behavior. Investigations into the electronic structure of TS_2 compounds is important for an understanding of the catalytic mechanisms occurring at the surface. An understanding of the electronic structure at the catalyst surface is important when considering the interaction of an adsorbate with the catalyst surface. For example, in the formation of $\text{C}_1\text{-C}_4$ alcohols over Cs-doped MoS_2 , the electronic interaction of H_2 with the surface of MoS_2 is an important issue. The Cs-doped MoS_2 system has been extensively studied in terms of catalytic activity but little is known about the method in which hydrogen is activated on the surface. Electronic studies characterizing the surface properties of MoS_2 may shed some light on the nature of hydrogen activation.

A good experimental method of studying trends in the electronic structure of disulfide surfaces is by core level and valence band analysis *via* high resolution electron spectroscopy for chemical analysis (HR-ESCA), also called high resolution X-ray photoelectron spectroscopy, HR-XPS. HR-ESCA is a surface sensitive technique that can provide information on the oxidation state and chemical environment of surface species. Analysis of the valence bands *via* HR-ESCA can also lead to information on the highest occupied

bands, which will most likely interact with specific adsorbates such as H_2 . In general, since the TS_2 compounds are fairly covalent, the valence bands obtained *via* HR-ESCA are combinations of the atomic valence levels of sulfur and the transition metal. The experiment does not resolve the valence band into contributions due to the atomic valence levels from different atoms. Theoretically calculated valence bands can be used to interpret the HR-ESCA experimental results. A solid state adaptation of the extended Hückel theory is a very simple method that will calculate the density of states, as well as the contributions of the valence atomic orbitals to the density of states. As pointed out in the Experimental Section, the computational package used for these calculations was the "Extended Hückel Molecular, Crystal and Properties Package" [83]. This theory has been used to calculate the valence bands of representative transition metal disulfides, with some encouraging initial results. Thus, trends in the electronic structure of the disulfides can be studied in detail. Surface band structure can be theoretically investigated by setting up models with translational periodicity parallel to the surface, with the surface atoms in their regular or relaxed lattice positions, and the theory compared with experimentally determined band structures.

The computational program gives a density of states that cannot be compared directly to the valence band obtained *via* HR-ESCA. The ability of photoelectrons to be detected in the instrument depends on the incident X-ray energy and the atomic level and specific atom type from which the photoelectron originates. Thus, the experimental valence band could be considered to be a density of states modified by the photoelectron cross-sections of the atomic orbitals. Therefore, a theoretical valence band must be compared to the experimental valence band. A theoretical valence band can be obtained from the atomic orbital population (AOPOP) contributions to the density of states (DOS). These atomic

orbital contributions (AOPOP's) are multiplied by their corresponding photoelectron cross-sections to obtain modified AOPOP's (MAOPOP). The modified AOPOP's are then summed at each energy to obtain the theoretical valence band that can be compared directly to experiment. In the case of MoS_2 , the Mo 4d to S 3p photoelectron cross-section ratio is 4.08. Therefore, the Mo 4d AOPOP will be multiplied by a factor of 4.08 as compared to the S 3p AOPOP, resulting in a large contribution of the Mo 4d atomic orbitals to the valence band region.

The experimental HR-ESCA valence band regions of MoS_2 and NbS_2 are shown in Figure 17 and 18, respectively. The difference in the two disulfides can be seen immediately at the top of the valence band. The intensity of the peak at the top of the NbS_2 valence band relative to the rest of the valence band is less than in the case of MoS_2 . NbS_2 (Nb^{+4} , d^1 system) is a metal and has the highest occupied crystal orbital (HOCO) only half-occupied. MoS_2 (Mo^{+4} , d^2 system) is a small band gap semiconductor and has the HOCO fully occupied by electrons. Theoretical valence bands that have been parametrized and modified by the photoelectron cross-sections are shown in Figure 19 and 20 for MoS_2 and NbS_2 , respectively. The theoretical valence bands reproduce the experimental valence bands very well. The dispersion of the S 3s region is in good agreement between theory and experiment. The four-peaked nature and width of the upper portion of the valence band is reproduced theoretically. From experience manipulating the program, it has been found that the most important feature in obtaining an accurate description of the upper portion of the valence band is the radial extent of the S 3p atomic orbitals. If the S 3p Slater-type atomic orbitals are not highly diffuse, small overlap between the S 3p and Mo 4d atomic orbitals in the MoS_2 lattice will result in a 3-peaked valence band. However, more diffuse S 3p atomic orbitals produce the required overlap needed to give the valence band its 4-

FIGURE 17

Valence band region of polycrystalline MoS₂ shifted by 4.12 eV (work function, 4.1 eV; calibration, 0.02 eV).

Pass energy
75 eV

Slit width
1.1 mm

Energy step
0.05 eV

Det. height
60 %

Lens mode
TRANSMISSION

X-ray power
4.0 kW

Rec. time
03: 23: 16

SCIENTA

FIGURE 18

Polycrystalline NbS(2-x), Valence Band Region.
VALENCE1 LEHIGH

Pass energy
75 eV

Slit width
1.1 mm

Energy step
0.05 eV

Det. height
90 %

Lens mode
TRANSMISSION

X-ray power
7.4 kW

Rec. time
04: 11: 32

SCIENTA

FIGURE 19

Valence band region of polycrystalline MoS₂ shifted by 4.12 eV (work function, 4.1 eV; calibration, 0.02 eV).

SCIENTA

FIGURE 20

Polycrystalline NbS(2-x), Valence Band Region.
VALENCE1 LEHIGH

Pass energy
75 eV

Slit width
1.1 mm

Energy step
0.05 eV

Det. height
90 %

Lens mode
TRANSMISSION

X-ray power
7.4 kW

Rec. time
04:11:32

SCIENTA

peaked nature. On comparison of the theoretical valence bands of MoS_2 and NbS_2 a question might arise as to the difference in the dispersion of the S 3s region. In MoS_2 , the theoretical dispersion is greater because of the smaller lattice constant, 3.16 Å, that separates the sulfur atoms within each S atomic layer. In NbS_2 , the theoretical dispersion is smaller because of the larger lattice constant, 3.31 Å, that separates the sulfur atoms within each S atomic layer.

A better understanding of the experimental valence band can be achieved by analysis of the theoretical MAOPOP's. Shown in Figure 21 are the modified AOPOP's (Mo 4d, S 3s, and S 3p) for MoS_2 . Thus, the S 3s atomic orbitals are mainly the cause of the dispersion of the peak located at approximately 17.8 Ev. The top of the valence band and (HOCO) located at approximately 6.0 Ev is made up mainly of Mo 4d character. This character is usually referred to as d_{z^2} . However, an analysis of the atomic orbital coefficients that make up the crystal orbitals shows that the Mo 4d AOPOP consists of a considerable amount of $d_{x^2-y^2}$ and d_{xy} as well as d_{z^2} character. The covalent nature of MoS_2 can be seen in the large amount of mixing in the remainder of the valence band between the S 3p and Mo 4d atomic orbitals.

Now that the electronic structure of the bare MoS_2 surface has been investigated theoretically, predictions as to probable adsorption sites can be made. Studies under way at this time involve the adsorption of hydrogen on the MoS_2 surface both theoretically and experimentally. The latter studies are centered on HR-XPS, and TPD studies should also be carried out. Theory, when compared to experiment, will lead to the identification of catalytic activation sites and insight into the mechanism of hydrogen adsorption. Subsequent studies are needed on the alteration of the electronic properties of MoS_2 upon surface doping with alkali and the influence that this has on the adsorption of CO.

FIGURE 21

Theoretical Valence Band
2-D MoS₂ (#171 kp)

Catalytic Testing of Cs/MoS₂ Catalysts

Air-Doped CsOOCH/MoS₂ = 20/80 wt% Catalyst. This testing program utilized the 20 wt% CsOOCH/MoS₂ catalyst that was doped in air as described in the Experimental Section. Three catalytic tests were carried out with this catalyst, and they consisted of the following:

1. Testing with H₂/CO = 1/1 synthesis gas,
2. Initial testing with synthesis gas containing 45.4 ppm H₂S, and
3. Temperature dependence of the H₂S effect.

A 1.5365 g portion of the calcined CsOOCH/MoS₂ = 20/80 wt% catalyst that was prepared in air was mixed with approximately 10 ml of 3 mm Pyrex beads. This mixture was then centered in a 316 stainless steel fixed bed reactor using additional quantities of the Pyrex beads. No effort was made to keep the catalyst from contacting air. Pretreatment of the catalyst was carried out at 0.1 MPa by passing a 2.04/97.96 mol% H₂/N₂ mixture. After the flow rate of 60 ml/min was attained, the catalyst was heated to 410°C and this temperature was maintained for one hr. The reactor was then allowed to cool to room temperature overnight under the hydrogen/nitrogen flow. The gas flow was then changed to the H₂/CO = 1/1 synthesis gas mixture and the reactor was then pressurized to 8.3 MPa. With the CO/H₂ synthesis gas at a gas hourly space velocity (GHSV) of 7810 ℓ/kg cat/hr, catalytic testing was carried out at the temperatures of 245, 265, 285, and 310°C.

As shown in Table 9 and Figure 22, the catalyst was more active at higher temperatures and was more selective to alcohols than to hydrocarbons over the entire temperature range. As expected, as the temperature was increased the selectivity toward alcohols decreased, while the selectivity toward hydrocarbons increased, as shown in Figure 23, where the selectivities are expressed on a CO₂-free basis. This agrees with observations

FIGURE 22. Product Yield vs Temperature
at 8.3 MPa with $\text{H}_2/\text{CO} = 1/1$ Synthesis
Gas with GHSV = 7810 l/kg cat/hr

FIGURE 23. Product Selectivity as a Function of Temperature at 8.3 MPa with $H_2/CO = 1/1$ with GHSV = 7810 l/kg cat/hr

obtained in earlier work [11,65,87]. At the same time, the methanol/ethanol molar ratio decreased with increasing temperature, indicating that higher reaction temperatures enhance higher alcohol formation.

TABLE 9. Product space time yields (g/kg catal/hr) obtained over the 20 wt% CsOOCH/MoS₂ catalyst with H₂/CO = 1/1 synthesis gas at 8.3 MPa and with GHSV = 7810 ℓ/kg cat/hr.

Temp. (°C)	CH ₄	CO ₂	Methanol	Ethanol
245	3.1	14.2	38.9	0.0
265	18.6	52.6	107.9	31.8
285	31.0	87.5	120.7	52.2
310	46.0	122.5	138.0	71.6

The second part of the testing program with the 20 wt% CsOOCH/MoS₂ catalyst involved testing with synthesis gas containing 45.4 ppm H₂S. The purpose of this experiment was to investigate the report by Dow Chemical Co. [88] that hydrogen sulfide in the synthesis gas makes alkali promoted molybdenum disulfide alcohol synthesis catalysts more selective to higher alcohols, although the Cs-doped MoS₂ catalyst was not studied by the researchers at Dow Chemical Co. The present experiment was carried out using the same catalyst as employed in the previous experiment; it was not unloaded from the reactor and was not pretreated again. A GHSV of 7810 ℓ/kg cat/hr again was used with a CO/H₂ ratio of 1.0. A 91 ppm hydrogen sulfide in hydrogen mixture was used for the experiments in which the H₂S was introduced into the reactant synthesis gas stream. Therefore, there was 45.5 ppm of H₂S passing over the catalyst. Several temperatures and pressures were investigated in this initial screening of the catalyst, as described below.

To monitor if the presence of hydrogen sulfide was having an effect on the selectivity of higher alcohols, the ratio of methanol/ C_2^+ alcohols was used as an indicator. If the hydrogen sulfide had an effect as reported, the ratio would decrease. It was observed that at lower temperatures, the presence of H_2S in the reactant did have an effect. For example, at 8.3 MPa and 285°C the methanol/ C_2^+ alcohol molar ratio dropped from 6.76 for no H_2S added to 3.76 when H_2S was added, as indicated in Table 10. The effect occurred immediately upon addition of the hydrogen sulfide, and it was accompanied by a small decrease in the total alcohol yield and a small increase in the hydrocarbon (HC)/alcohol ratio. These changes were not systematic at higher temperatures and higher pressures, and should be investigated in better designed experiments in the future.

TABLE 10. Alcohol Yields and Product Molar Ratios over the Cs/MoS₂ = 20/80 wt% Catalyst from $H_2/CO = 1$ Synthesis Gas at GHSV = 7810 ℓ/kg cat/hr.

Pressure (MPa)	Temp. (°C)	H ₂ S (Y/N)	Methanol/ C ₂₊ Alcohols Ratio	HC/ Alcohol Ratio	Alcohol Yield (g/kg/hr)
8.3	285	N	6.76	0.15	167
8.3	285	Y	3.76	0.23	151
8.3	300	Y	2.49	0.25	200
8.9	325	Y	2.35	0.45	213
8.9	340	Y	1.47	0.78	227
8.9	350	Y	1.43	0.73	236
10.3	285	N	2.46	0.39	82
10.3	325	N	1.50	0.38	120
10.3	325	Y	1.85	0.52	181
10.3	350	N	1.44	0.75	228
10.3	350	Y	1.53	0.63	236

To probe the effect of residence time on the product yields and selectivities, different reactant flow rates were investigated at 10.3 MPa and 350°C with hydrogen sulfide in the gas stream. At the lowest flow rate with GHSV of 6500 ℓ /kg cat/hr at this high temperature and pressure, a high yield of methane relative to the alcohols was observed, Figure 24. However, as the flow rate was increased, an appreciable drop in methane yield occurred, and this resulted in an increased selectivity to alcohols.

A series of additional experiments was carried out in which the effect of temperature on the product yields and selectivities in the presence or absence of H_2S in the synthesis gas reactant was investigated. Utilizing $H_2/CO = 1/1$ synthesis gas at 8.9 MPa and with a GHSV of 7810 ℓ /kg cat/hr, the reaction temperature was varied in the sequence 285, 300, 310, 340, and 350°C using the same catalyst from the previous experiments. Steady state testing at each temperature was generally maintained for 3-4 hr before changing the reaction conditions.

Upon initiating this series of experiments, it appeared that the catalyst has deactivated because the yields of the total alcohols, indeed for all the product components, were substantially lower than in the initial experiments, e.g. compare Figure 25 with Figure 22. This apparent deactivation might be due to the higher temperature testing, i.e. 350°C, that had been carried out. During testing under lower temperature conditions, it had previously been shown that a 10 wt% K_2CO_3 doped Co-MoS₂ catalyst did not exhibit any deactivation during a 400 hr test at 8.3 MPa and 305°C with $H_2/CO = 0.96$ synthesis gas with GHSV = 3600 ℓ /kg cat/hr, which involved intermittent testing to 325°C [89].

At each reaction temperature, steady state product analyses by gas chromatography were collected and averaged before, during, and after hydrogen sulfide addition to the

FIGURE 24. Product Yields vs Reactant Flow Rate at 350°C and 10.3 MPa in the Presence of 45.5 ppm H₂S

FIGURE 25. Total Alcohol Yield vs Temperature at 8.9 MPa and GHSV = 7810 l/kg cat/hr with $H_2/CO = 1$

synthesis gas. The effect of temperature on the total alcohol yield seemed to be more pronounced than the effect of the presence or absence of H_2S , as shown in Figure 25. However, as the total alcohol yield was increasing with increasing temperature, the selectivity toward methanol was decreasing, see Figure 26. At the same time, the overall selectivity to C_2^+ alcohols increased from 285°C to 300°C , but it then remained rather constant, as shown in Figure 27. The reason for this is the increasing yields of hydrocarbons with increasing temperature, and this is shown as the molar ratio of hydrocarbons to alcohols in Figure 28.

As was found in a previous experiment, the hydrogen sulfide had the strongest effect at lower temperatures, e.g. on the methanol/ C_2^+ alcohol ratio. The significant H_2S effect on increasing the yield of the C_2^+ alcohols relative to methanol at 285°C is shown in Figure 29. At higher temperatures, it appeared that the presence or absence of H_2S had less of an effect on the methanol/ C_2^+ alcohols molar ratio than did the temperature.

The H_2S hardly affected the carbon dioxide yield, while at higher temperatures the hydrogen sulfide tended to lower the total alcohol yield (Figure 25). Of note is that at the higher temperatures, the H_2S also tended to lower the methane production (Figure 30). This causes a lowering of the hydrocarbon/alcohol molar ratio even though the total alcohol yield was also lowered. This effect would warrant further study if these high reaction temperatures were to be employed to achieve the higher C_2^+ alcohol/methanol ratio product composition. Without the presence of H_2S , the higher temperatures increase the yield of methane in a more pronounced manner.

FIGURE 26. Dependence of the Methanol Selectivity on Reaction Temperature at 8.9 MPa and GHSV = 7810 l/kg cat/hr

FIGURE 27. Selectivity of C_2^+ Alcohols
vs Temperature at 8.9 MPa and GHSV =
7810 l/kg cat/hr with $H_2/CO = 1$

FIGURE 28. Hydrocarbon/Alcohol Molar Ratio from $H_2/CO = 1$ Synthesis Gas at 8.9 MPa and 7810 l/kg cat/hr

FIGURE 29. Methanol/C₂⁺ Alcohol Molar Ratio vs Temperature from H₂/CO = 1 at 8.9 MPa and 7810 l/kg cat/hr

FIGURE 30. Methane Yield vs Reaction Temperature with $H_2/CO = 1$ at 8.9 MPa and GHSV = 7810 l/kg cat/hr

Catalytic Testing of Undoped Molybdenum Disulfide. In a nitrogen-filled glove bag, 1.6567 g of undoped MoS₂ from large Batch 1 (Pretreatment B) was mixed with $\approx$ 8 ml clean Pyrex beads and centered in the reactor. After connecting the reactor to the catalyst testing unit, the MoS₂ catalyst was reductively pretreated at 400°C with 2.04 vol% H₂/97.96 vol% N₂ (60 ml/min) for 1 hr at ambient pressure before testing.

Catalytic testing was carried out at a pressure of 8.1 MPa with a gas hourly space velocity (GHSV) of 7750 ℓ /kg cat/hr at the following temperatures 245, 255, 265, 275, 280, 300, and 320°C. For each temperature change, the reaction was allowed to reach steady state, and then testing was maintained under constant reaction conditions for 4 to 12 hr. As expected, the reaction over MoS₂ only produced hydrocarbons, water, and carbon dioxide. At lower temperatures, the major product was methane. As the reaction temperature was sequentially increased, higher molecular weight products were formed (up to C₆). Other trends that were seen included the observation that as the temperature was increased, the conversion of CO tended to increase, as can be seen in Figure 31. During this test, the CO₂/H₂O molar ratio also increased with increasing temperature, as shown in Figure 32. This increase in the CO₂/H₂O molar ratio occurred because the equilibrium of the water gas shift reaction, Equation 15, was shifted to the H₂ + CO₂ side as the temperature was increased.

Since C₁-C₆ hydrocarbon products were formed at the higher reaction temperatures, Schulz-Flory distribution plots were made for each of the higher temperatures used. These plots are shown in Figures 31-36. In constructing these graphs, Equation 16 was utilized and the log of the product concentration, given in terms of mol/hr, was plotted vs the carbon

FIGURE 31. CO Conversion (mol/kg cat/hr)
vs Temperature Over MoS₂ at
8.1 MPa and GHSV = 7750 l/kg cat/hr

FIGURE 32. $\text{CO}_2/\text{H}_2\text{O}$ Molar Ratio
vs Temperature at 8.1 MPa and
GHSV = 7750 l/kg cat/hr with $\text{H}_2/\text{CO} \approx 1$

FIGURE 33. Schulz-Flory Plot
for MoS_2 at 265°C , 8.1 MPa,
and GHSV = 7750 l/kg cat/hr

FIGURE 34. Schulz-Flory Plot
 at 280°C, 8.1 MPa, and GHSV =
 7750 l/kg cat/hr

FIGURE 35. Schulz-Flory Plot
at 300°C, 8.1 MPa, and GHSV =
7750 l/kg cat/hr

FIGURE 36. Schulz-Flory Plot
for MoS_2 at 320°C , 8.1 MPa ,
and $\text{GHSV} = 7750\text{ l/kg cat/hr}$

number (n) of that product. For normal carbon-carbon bond formation *via* addition of a C₁ unit to a growing C_n carbon chain according to polymerization kinetics, this should give a straight line with a negative slope. The slope of the line expresses the probability of carbon chain growth and is designated as being equal to the log of α , where α is expressed as shown by Equation 17.

$$\log C_n = 2 \log (\ln \alpha) + n \log \alpha \quad (16)$$

$$\alpha = k_p / (k_p + k_t) \quad (17)$$

Equation 17 relates the probability that any intermediate carbon chain will grow by propagation rather than terminating *via* hydrogenation and desorption, where k_p is the rate for the propagation reaction and k_t is the rate of termination. The α value for each reaction was determined from the least squares best fit of the data at each reaction temperature from the Anderson-Schulz-Flory distribution of products. An appreciable scatter in the value of α was obtained, but no large variation of α was noted, as shown in Table 11. Table 12 shows that higher molecular weight products were produced at higher reaction temperatures, indicating that propagation was more likely at the higher temperatures. This can be seen in Figure 37, where the space time yields of all of the hydrocarbon products increased with increasing reaction temperature. However, there were appreciable variations in the C₂-C₄ product space time yields at the temperatures of 265, 280, and 300°C.

After the above tests were conducted, the temperature was decreased to 295°C, and methanol was injected into the inlet synthesis gas at a rate of 18 μ l/min using the high pressure Gilson pump. This experiment was carried out to determine if the undoped MoS₂ catalyst would homologate the methanol into ethanol. No oxygenates were observed during

the pumping of methanol. However, it was observed that the methanol was decomposed to carbon monoxide and hydrogen, and higher yields of hydrocarbons were obtained (Figure 38).

TABLE 11. Experimentally Determined Alpha Values

TEMPERATURE (°C)	SLOPE	ALPHA
265	-0.621	0.239
280	-0.508	0.310
300	-0.540	0.288
320	-0.589	0.258

TABLE 12. Product space time yields (g/kg cat/hr) of the hydrocarbons, carbon dioxide, and water formed over the updoped MoS₂ catalyst from H₂/CO = 1/1 synthesis gas.

TEMP (°C)	CH ₄	C ₂	C ₃	C ₄	C ₅	C ₆	CO ₂	H ₂ O
245	23.2	0	0	0	0	0	3.6	45.2
255	15.3	0	0	0	0	0	5.8	40.5
265	12.0	2.2	3.4	0	0	0	8.8	23.3
280	20.7	72.4	20.5	2.6	0	0	16.1	92.4
300	57.9	3.0	8.8	7.3	0	0	44.6	91.8
320	303.9	75.6	30.4	19.8	5.2	1.2	87.0	65.3

FIGURE 37. Space Time Yield vs Temperature at 8.1 MPa and GHSV = 7750 l/kg cat/hr Over MoS₂

FIGURE 38. Schulz-Flory Plot
for MoS_2 at 295°C , 8.1 MPa,
and GHSV = 7750 l/kg cat/hr

Testing of 13 wt% CsOOCH/MoS₂. This promoted catalyst was loaded into the reactor and pretreated in the same manner as described earlier for the undoped MoS₂. The testing was carried out at 8.1 MPa with H₂/CO = 1 synthesis gas at a GHSV of 7750 ℓ/kg cat/hr at 245, 255, 265, 275, 285, and 295°C. After this set of temperatures was run, the reaction was run at 245°C again to determine if there was any deactivation of the catalyst. As can be seen in Figure 39, which is a plot of the space time yield of methane vs time of testing, there was apparent deactivation at each of the higher reaction temperatures, as well as by comparing the initial test and the final test at 245°C. A plot of the total space time yield of oxygenates (alcohols + esters) exhibited very similar behavior, but there was more scatter in the experimental data at each temperature. The data in Figure 39 were collected during approximately 100 hr of continuous testing. Prior to Sample No. 94, the furnace was turned off and the reactor was allowed to cool to 245°C, at which point a rather constant reactor temperature of 245°C was maintained at the end of the experiment.

During this testing program at temperatures of 275°C and higher, apparent deactivation can be seen from the gradual decline in methane formation with time. The products that were formed in the reaction in appreciable yields in addition to methane were methanol, ethanol, propanol, ethyl formate, water, and carbon dioxide. The general trends that were followed by the catalyst were increasing selectivity of hydrocarbons, principally methane, and decreasing selectivity to alcohols with increasing temperature (Figure 40), which is also shown in Figure 41 where the hydrocarbon/alcohol molar ratio increased with increasing reaction temperature. As the temperature was increased, more higher alcohols were formed relative to methanol, and this is shown in Figure 42 where the methanol/C₂⁺ oxygenated products molar ratio decreases with increasing temperature. As expected, the space time yields of the products increased with increasing reaction temperature (Figure 43).

FIGURE 39. Methane Productivity vs Time

FIGURE 40. Selectivity vs Temperature
Over the Cs/MoS₂ Catalyst

FIGURE 41. Hydrocarbon/Alcohol
Molar Ratio Over Cs/MoS₂

FIGURE 42. Methanol/ C_2^+
Oxygenated Products Molar Ratio

FIGURE 43. Space Time Yield of Products Over Cs/MoS₂ with H₂/CO = 1 vs Temperature at 8.1 MPa

Catalytic Testing of the 12.5 wt% K/MoS₂ Catalyst. After the doping of this catalyst from liquid ammonia solution with metallic potassium was achieved using the apparatus shown in Figure 13, the catalyst was loaded into the reactor under argon and a flow of H₂/CO = 0.99 synthesis gas was initiated with GHSV = 7796 ℓ/kg cat/hr (no reductive pretreatment was employed). The reactor was then pressurized to 8.3 MPa and heated slowly to 245°C. The formation of alcohols was first seen at ≈200°C. The products in the exit gas were analyzed every 25-30 min using an on-line Hewlett-Packard 5890 Series II GC, and condensable products were also collected for analysis by GC/MS.

During the early period of testing of this catalyst at 245°C, a new analytical method was developed in which the GC thermal conductivity detector sensitivity was switched from low sensitivity to high sensitivity after the unreacted CO eluted as a peak. Hydrogen was not quantitatively analyzed. A correlation factor was found so that the space time yields of all of the oxygenated and hydrocarbon products could be accurately determined during the later stage of this testing.

Quantitative analytical data were obtained during the later period of catalytic testing (after 585 hr of continuous low temperature testing) at reactor temperatures of 245, 256, 265, and 295°C. The product selectivities and space time yields are presented in Figures 44-47. In Figure 44 only the alcohol and hydrocarbon selectivities are shown, although there were also small amounts of esters and aldehydes present in the reaction products. The selectivity toward hydrocarbons, principally methane, increased from ≈10 C mol% at 245°C to ≈19 C mol% at 295°C. As the reaction temperature was increased, the space time yield of the alcohol portion of the product significantly increased, as shown in Figure 46. Figure 47 shows that the large increase in productivity of alcohols upon increasing the temperature to 295°C can be attributed principally to the enhanced formation of methanol.

FIGURE 44. SELECTIVITY (C mol%)
vs TEMPERATURE

FIGURE 45. CO₂ SPACE TIME YIELD
vs TEMPERATURE

FIGURE 46. TOTAL ALCOHOL AND
HYDROCARBON SPACE TIME YIELDS
vs TEMPERATURE

FIGURE 47. ALCOHOL SPACE TIME YIELDS vs TEMPERATURE

As the reaction temperature was increased, the conversion level of CO increased, as shown in Figure 48, corresponding to 4 mol% CO conversion at 295°C. Figure 49 shows that as the temperature was increased, an apparent minimum in the methanol/C₂+ alcohol molar ratio, based on the moles of products formed, was observed. In contrast, the total alcohol/hydrocarbon molar ratio exhibited a linear dependence on the reaction temperature, as shown in Figure 50. This latter behavior was expected since more hydrocarbons were formed at higher reaction temperatures (see Figure 44), where most of the hydrocarbon product consisted of methane.

In this investigation, the promoted MoS₂ catalyst initially contained metallic potassium, and this experimental testing shows that alcohol synthesis catalysts can be successfully synthesized utilizing this new preparation method. The catalytic results, where a total testing time of over 700 hr was utilized, show that a stable catalyst was obtained. Further characterization of this catalyst is needed.

Testing of the 10 wt% CsOOCH/MoS₂ Catalyst. Batch 3 MoS₂, with a surface area of 60 m²/g, was doped with CsOOCH under vacuum, and then the dried catalyst was weighed and transferred to the reactor in air. A 1.1290 g portion of the 10% CsOOCH/MoS₂ catalyst was mixed with approximately 15 ml of 3 mm Pyrex beads. This mixture was then centered in a 316 stainless steel fixed bed reactor using additional quantities of the 3 mm Pyrex beads. After the reactor was reassembled, the catalyst was pretreated at 410°C for 1 hr under a flow of 2.04/97.96 H₂/N₂ vol% mixture at a flow rate of 60 ml/min. The reactor was then allowed to cool to room temperature overnight while maintaining the hydrogen/nitrogen flow. The gas flow was then changed to the H₂/CO = 1 synthesis gas reactant mixture, and the reactor was pressurized to 8.1 MPa, the gas hourly space velocity (GHSV) was adjusted to 7750 ℓ/kg cat/hr, and then heated at a steady rate

FIGURE 48. CO CONVERSION RATE
(mol/kg cat/hr) vs TEMPERATURE

FIGURE 49. METHANOL/C₂+ ALCOHOL
MOLAR RATIO vs TEMPERATURE

FIGURE 50. ALCOHOL/HYDROCARBON
MOLAR RATIO *vs* TEMPERATURE

to the initial reaction temperature.

Catalytic testing was carried out in which two series of increasing reaction temperatures were utilized. These two sets of temperatures consisted of the following:

Temperature Set 1: 245, 256, 285, 295, 300, 308, 310, and 350°C, and.

Temperature Set 2: 265, 275, 288, 340, 285, and 245°C.

The second set of temperatures was run directly after the first set of temperature. It is pointed out that the higher reaction temperatures of 350 and 340°C are fairly severe conditions for alcohol synthesis catalysts. As will be shown in the figures in this report, there was a difference between the two sets of temperatures. This indicated that the catalyst deactivated over time. This was especially pronounced after lowering the temperature to 245°C at the end of the *second* temperature sequence. Indeed, while there was activity at this temperature at the beginning of the testing sequence, there was no activity observed at the end of the second reaction series that terminated at 245°C. The testing at each temperature was maintained at steady state for 6-24 hr, during which multiple analyses of the product stream were carried out. The catalytic response to a temperature change was immediate.

Some of the observed catalytic trends in terms of activity and selectivity are summarized here. Upon increasing the temperature according to **Temperature Set 1**, the productivity of methanol, which was the dominant product, proceeded through a broad maximum, as shown in Figure 51. As expected, the selectivity of the alcohols decreased as the temperature increased, while the selectivity of the hydrocarbons increased as the temperature increased for Temperature Set 1. These trends are shown in Figures 52 and 53 for the 285-350°C temperature range. Indeed, at 350°C the product selectivity was greatly shifted to the hydrocarbon, as shown in Figure 53. This behavior, however, was surprisingly

FIGURE 51. Product Space Time
Yield vs Temperature (Set 1) at
8.1 MPa, 7750 l/kg cat/hr, H₂/CO = 1

FIGURE 52. Selectivity vs Temperature
(Set 1) at 8.1 MPa and GHSV =
7750 l/kg cat/hr with $H_2/CO = 1$

FIGURE 53. Selectivity vs Temperature
(Set 1) at 8.1 MPa and GHSV =
7750 l/kg cat/hr with $H_2/CO = 1$

not observed during the Temperature Set 2 testing sequence. As the reaction temperature was progressively increased, the space time yield of methanol also increased, shown in Figure 54, and the selectivity trends were now reversed compared with the first set of experiments. As shown in Figures 55 and 56, the selectivity towards alcohols during the second set of experiments improved as the reaction temperature was increased. This is unexpected behavior for this catalyst. In each case, the selectivities were calculated on a CO- and CO₂-free basis.

Although there is scatter in the data, the conversion of CO in mol% and mol/kg cat/hr increased with increasing temperature for both series of experiments, as shown in Figures 57 and 58, respectively. The extent of deactivation of the CsOOCH/MoS₂ catalyst after the first testing sequence that reached 350°C is indicated in these figures, where the solid lines are computer-drawn trend lines that neglect the final 245°C data point (no activity). Of special interest is the alcohol productivity of this catalyst in terms of %yield and space time yield of the alcohols, and these are shown in Figures 59 and 60, respectively, as functions of the reaction temperature.

While the catalyst behavior in alcohol productivity as a function of temperature is of great interest (shown in Figure 60), correlation of the hydrocarbon/alcohol molar ratio during these experiments is also of interest. As shown in Figure 61, the product hydrocarbon/alcohol molar ratio was fairly constant in the 285-310°C temperature range during Temperature Set 1 testing but then increased above 1.0 when the reaction temperature was increased to 350°C. The latter point indicates an exceptionally large quantity of hydrocarbon products formed. However, under Temperature Set 2 conditions, the ratio decreased as the temperature increased (Figure 61). This latter observation is the opposite of the expected behavior, and it cannot be explained without further studies.

FIGURE 54. Product Space Time
Yield vs Temperature (Set 2) at
8.1 MPa, 7750 l/kg cat/hr, H₂/CO = 1

FIGURE 55. Selectivity vs Temperature
(Set 2) at 8.1 MPa and GHSV =
7750 l/kg cat/hr with $H_2/CO = 1$

FIGURE 56. Selectivity vs Temperature
(Set 2) at 8.1 MPa and GHSV =
7750 l/kg cat/hr with $H_2/CO = 1$

FIGURE 57. Conversion of CO
in Mol% vs Reaction Temperature

FIGURE 58. Conversion Rate of CO vs Reaction Temperature

FIGURE 59. Total Alcohol % Yield
vs Temperature at 8.1 MPa and
GHSV = 7750 l/kg cat/hr with $H_2/CO = 1$

FIGURE 60. Total Alcohol Space Time Yield vs Temperature at 8.1 MPa and GHSV = 7750 l/kg cat/hr with $H_2/CO = 1$

FIGURE 61. Hydrocarbon/Alcohol Molar Ratio vs Temperature from $H_2/CO = 1$ at 8.1 MPa and 7750 l/kg cat/hr

The alcohol productivity of this catalyst at 295°C during the Set 1 experiments appeared to be anomalously low compared to the 285, 300, and 310°C testing results. For example, the total alcohol productivities at these temperatures were 136.2, 138.8, and 135.3 g/kg cat/hr, respectively. Over an earlier tested 10 wt% CsOOCH/MoS₂ catalyst [11,65], the alcohol productivity under approximately the same reaction conditions was ≈240 g/kg cat/hr. Therefore, the present catalyst is significantly less active than the 10/90 wt% CsOOCH/MoS₂ catalyst prepared earlier [11,65]. Although this is a low activity catalyst, the experiments indicate that partial deactivation tended to increase the yield of hydrocarbon at lower reaction temperatures but to lower the productivity of the hydrocarbons at higher reaction temperatures. Further work is need to understand this catalytic behavior.

Testing 10 wt% CsOOCH/MoS₂ Catalyst-Sample 2. A second sample of 10 wt% CsOOCH/MoS₂ catalyst was tested, and the sample was protected against air exposure during its preparation steps. This catalyst was Sample 2, as designated in the Experimental Section, and it was prepared by decomposing undiluted MoS₃ in a N₂ flow, transferring to a vacuum apparatus (Figure 12), and doping with CsOOCH. The catalyst (1.7313 g) was mixed with Pyrex beads and loaded into the reactor under N₂ to form a bed approximately 12 cm in height in the reactor. The catalyst was reductively pretreated with H₂/N₂ = 2/98 vol% gas flowing at 60 ml/min. The temperature was slowly increased to 400°C, and CO₂ and H₂O were monitored by gas chromatography, while H₂S was monitored by lead acetate paper. Hydrogen sulfide was first detected at 191°C and was still present in the exit gas after 1 hr of pretreatment, at which time the temperature was decreased to ambient conditions. No H₂O nor CO₂ was detected. After cooling, the catalyst was maintained in the H₂/N₂ mixture overnight prior to catalytic testing.

After setting the $\text{H}_2/\text{CO} = 1/1$ synthesis gas flow rate to $\text{GHSV} = 7758 \text{ l/kg cat/hr}$, the reactor was pressurized to 8.3 MPa and then heated to 245°C. The reaction temperature was then increased sequentially to 256, 265, 275, and 295°C. The exit stream was sampled and analyzed every 33 min using an on-line GC. Liquid products were also collected for GC/MS analyses.

Steady state conversions were maintained for 20-40 hr at each reaction temperature, as shown in Figure 62. The CO conversion at 265°C corresponded to 4.7% conversion to products. As the reaction temperature was progressively increased, the productivities of the alcohols, hydrocarbons, and carbon dioxide increased, as shown in Figures 63 and 64. A high productivity to linear alcohols was observed at 295°C, as indicated in Figure 63. At each temperature, the dominant alcohol formed was methanol, compare Figure 65 with Figure 63.

At all temperatures, the alcohols were the principal products. However, a significant selectivity toward hydrocarbon formation, typical for alkali/ MoS_2 catalysts, was observed, as shown in Figure 66. This is further reflected by the plot shown in Figure 67 of the alcohol/hydrocarbon molar ratio for the products formed at each temperature. The average space time yields of the alcohols and total hydrocarbons are shown in Figures 68 and 69. There was hardly any noticeable trend toward the formation of higher molecular weight alcohols relative to methanol as the reaction temperature was increased, see Figure 70.

This $\text{CsOOCH}/\text{MoS}_2 = 10/90 \text{ wt\%}$ catalyst was an active catalyst, and this is demonstrated by the data in Table 13. The comparison with a previously tested catalyst [11], included in Table 13, shows that the present catalyst was slightly less active at lower reaction temperatures but slightly more active at higher temperatures. Some apparent deactivation occurred at 295°C, see Figures 62 and 65. Upon returning to a reaction

FIGURE 62. CO CONVERSION RATE VS TIME

FIGURE 63. TOTAL ALCOHOL AND HYDROCARBON SPACE TIME YIELDS VS TIME

FIGURE 64. CARBON DIOXIDE SPACE
TIME YIELDS VS TIME

SPACE TIME YIELD(g/kg cat/hr)

FIGURE 65. METHANOL SPACE TIME
YIELDS VS TIME

FIGURE 66. SELECTIVITY (C MOLE%)
VS TEMPERATURE

FIGURE 67. ALCOHOL/HYDROCARBON
MOLAR RATIO VS TEMPERATURE

FIGURE 68. TOTAL ALCOHOL AND HYDROCARBON
SPACE TIME YIELDS VS TEMPERATURE

FIGURE 69. ALCOHOL SPACE TIME
YIELDS VS TEMPERATURE

FIGURE 70. METHANOL/C₂+ ALCOHOL
MOLAR RATIO VS TEMPERATURE

TABLE 13. Comparison of product space time yields (g/kg cat/hr) and CO conversion rates (mol CO/kg cat/hr) for (A) the present 10 wt% CsOOCH/MoS₂ catalyst with (B) those reported earlier [11,65] for a catalyst of the same composition under the same reaction conditions.

PRODUCT	245°C	256°C	265°C	275°C	295°C	Catalyst
Carbon Dioxide	55.48 52.47	75.48 79.74	113.69 136.83	159.06 166.66	273.71 317.10	A B
Water	-- tr	-- tr	-- tr	-- 0.49	1.59 3.66	A B
Methane	7.03 12.75	9.21 16.73	14.61 26.31	23.08 31.50	42.87 62.00	A B
Ethylene	0.79 0.28	0.96 0.76	1.06 0.68	0.98 0.63	1.07 0.92	A B
Ethane	2.55 0.92	2.80 2.01	4.35 4.18	5.87 5.71	11.72 13.52	A B
Propane	tr --	1.37 0.28	1.55 1.03	1.07 1.87	5.63 6.77	A B
Butane	-- --	-- --	-- --	tr --	tr 2.76	A B
Methanol	53.67 85.32	83.22 106.22	119.18 132.71	168.87 141.04	192.50 152.86	A B
Ethanol	20.16 24.12	28.55 32.96	43.47 48.87	56.83 52.75	70.06 62.70	A B
1-Propanol	6.17 5.06	7.78 7.54	13.11 12.71	15.74 14.93	25.04 22.23	A B
1-Butanol	-- --	-- tr	1.42 tr	3.62 tr	5.86 3.63	A B
Methyl Formate	tr 0.86	0.95 1.20	1.88 1.03	2.52 1.54	2.62 tr	A B
Methyl Acetate	5.20 1.30	5.09 1.96	7.97 2.63	9.06 2.88	9.23 1.33	A B
Acetaldehyde	2.19 --	2.54 --	3.83 --	4.90 --	5.77 --	A B
Propanal	-- --	-- --	2.34 --	3.05 --	3.93 --	A B
CO Conversion Rate (mol/kg cat/hr)	3.83 4.53	5.23 6.06	7.77 8.63	10.76 9.74	14.67 14.09	A B

temperature of 245°C, a lower productivity for methanol was noted (Figure 65), but the CO conversion level was hardly affected (Figure 62). In contrast, the total alcohol productivity was now higher (Figure 63), and this reflects the enhanced space time yields of the higher alcohols. At the same time, the productivity of the hydrocarbons was suppressed.

The surface area of the undoped MoS₂ catalyst was determined to be 90 m²/g. The doped CsOOCH/MoS₂ catalyst exhibited a surface of 36 m²/g, which was appreciably higher than the value usually observed for fresh Cs-doped MoS₂ catalysts, as will be discussed later in this report. Upon catalytic testing, a still lower surface area is usually obtained.

X-Ray Powder Diffraction Analysis of MoS₂ Catalysts

The conversion of the precipitated and dried MoS₃ to MoS₂ by calcination is a highly exothermic reaction. This step is carried out in an 8 mm ID quartz tube about 60 cm long that is heated by a horizontal tube furnace. Our most recent preparations employed sample sizes consisting of 2-3 g of MoS₃ that were mixed with 3 mm Pyrex beads. This mixture was then centered in the tube by using additional layers of Pyrex glass wool and additional Pyrex beads. During the calcination process, a constant flow of helium, nitrogen, or other gas was maintained (typically 60 ml/min). The thermal program consisted of increasing the temperature up to 200°C quickly using a differential heating devise and holding for 10 min. Then the temperature was increased to 450°C for 1.5 hr, after which the sample was cooled in the flowing gas. As pointed out in the Experimental section, the sulfur released by the decomposition of the MoS₃ to form MoS₂ was condensed on Pyrex beads at the cool outlet of the tube.

It became evident that temperature control during the exothermic decomposition

reaction was difficult when large sample sizes were used. Thus, X-ray powder diffraction (XRD) characterization of the samples was carried out to monitor the purity and crystallite size of the MoS_2 . In addition, doping of the samples with cesium formate had been carried out, and XRD analysis of some of the Cs-doped samples was also carried out.

As described in the Experimental Section, two large batches of MoS_2 were prepared from two batches of MoS_3 that had been synthesized by coprecipitation from aqueous solution. The calcination of the MoS_3 was carried out using 2-3 g samples and the products of several of these portions were combined to form the two larger batches of MoS_2 . Figures 71 and 72 show the XRD patterns obtained for the two batches, which are designated as 2A (decomposition under He flow) and 1B (decomposition under N_2 flow). It is apparent that the patterns are nearly identical. The diffraction peaks exhibit appreciable width, which is indicative of small crystallite size of the MoS_2 .

A portion of the 1B batch of MoS_2 , as described in the previous technical progress report, was added to a measured quantity of an aqueous cesium formate solution, which was then evaporated to dryness under flowing nitrogen while maintaining constant stirring. The XRD pattern of the freshly prepared Cs/ MoS_2 catalyst, containing ≈ 10 wt% CsOOCH , is shown in Figure 73. The only dominant features in this pattern are the same MoS_2 diffraction lines as seen in Figures 71 and 72.

In contrast, a portion of the Cs/ MoS_2 sample prepared from the 2A batch of MoS_2 was allowed to stand in air for over three weeks before XRD analysis was carried out. The resultant XRD pattern is shown in Figure 74. By the presence of the new sharp diffraction line observed in the XRD pattern, it is evident that crystalline cesium formate has formed on the surface of the catalyst. From the sharpness of the lines, the CsOOCH crystallites are larger than 100 nm in diameter. It is proposed that upon standing in an ambient

FIGURE 71

Sample: 2A File: MD6J02.SM

FIGURE 72

Sample: 1B File: MD5J02.SM

FIGURE 73

Sample: 2B File: MD7J02.SM

FIGURE 74

Sample: 2a File: MD13.SM

atmosphere, the Cs dopant that had initially been present in a dispersed state has migrated, agglomerated, and crystallized into large particles of cesium formate. Thus, upon use under catalytic conditions for alcohol synthesis from H_2/CO synthesis gas, the cesium dopant would likely exist as a segregated component that would not provide the high conversion of reactants to alcohols that is desirable.

An additional series of experiments was carried out with a third batch of MoS_2 . After being prepared by calcination of MoS_3 , doping of the MoS_2 was carried out as for the samples described above to provide a doping level of ≈ 10 wt% $CsOOCH$. This sample was stored in a sealed vial, and the XRD pattern for the freshly prepared sample is shown in Figure 75. This sample was then allowed to stand in ambient atmosphere for a prolonged period of time (>1 month), and the resultant XRD pattern is shown in Figure 76. Very sharp strong diffraction lines for cesium formate are evident in Figure 76.

Catalytic testing of an analogous air-exposed 10 wt% $CsOOCH/MoS_2$ sample for alcohol synthesis from $H_2/CO = 1$ synthesis gas at 8.2 MPa and 295°C was carried out in the continuous flow gas phase reactor system ($GHSV = 7750$ l/kg cat/hr) after reductive pretreatment at 400°C in flowing 2.04 vol% $H_2/97.96$ vol% N_2 (60 ml/min) for 1 hr. Alcohols (dominant product) and hydrocarbons were formed, as expected, but the overall catalytic activity was only about half of that expected for the Cs doping level utilized with this catalyst. The XRD pattern of the tested catalyst is shown in Figure 77, and the presence of a small quantity of cesium formate in this sample is evident. Therefore, the catalyst samples used for catalytic testing should be freshly prepared and not allowed to stand in ambient atmospheres, i.e. those containing oxygen, water vapor, and carbon dioxide.

FIGURE 75

Sample: 130 File: MD10J03.SM

FIGURE 76

Sample: File: MD8J03.SM

FIGURE 77

Sample: USED File: MD9J03.SM

Surface Areas of the MoS₂-Based Catalysts

The surface areas of the catalysts were measured on a Gemini 2360 instrument using the BET multipoint method with nitrogen as the adsorbate. For the undoped MoS₂ catalyst, 10 data points were taken in the relative pressure range of $p/p_o = 0.05$ to $p/p_o = 0.30$ (see Figure 78), where p_o = saturated vapor pressure of N₂. For the rest of the samples, typically seven data points were obtained from $p/p_o = 0.05$ to $p/p_o = 0.30$ (e.g. see Figures 79 and 80). The plots show $z/[(1-z)V]$ vs z , where $z = p/p_o$, which are based on the BET equation of $p/[(p_o-p)V] = 1/V_m C + [(C-1)/(V_m C)]/(p/p_o)$, where V is the volume of gas adsorbed, V_m is the monolayer capacity, and C is the BET constant [90]. Multiplying V_m by the cross-sectional area of the N₂ molecule yields the specific surface area of the solid.

The surface areas of the undoped MoS₂ catalyst, the 20 wt% CsOOCH/MoS₂ catalyst prepared in air but before testing, and the Cs-doped catalyst after long-term testing were determined. These surface areas are compared with previously prepared and characterized catalysts in Table 14. The surface area of the undoped MoS₂ catalyst was found to be 60 m²/g. This is comparable to the previously reported [11] surface area of a different preparation of the undoped MoS₂ catalyst of 63 m²/g, which was obtained by heating MoS₃ in flowing N₂ to 500°C for 1 hr, using a heating rate of 10°C/min.

TABLE 14. Comparison of surface areas of the undoped MoS₂, untested 20 wt% CsOOCH/MoS₂, and tested 20 wt% CsOOCH/MoS₂ catalysts.

Catalyst	Surface Areas of Current Catalysts	Surface Areas of Earlier Catalysts [11]
MoS ₂	60	63
Untested Cs/MoS ₂	14	13
Tested Cs/MoS ₂	6	--

FIGURE 78. BET Plot
For Undoped MoS₂

FIGURE 79. BET Plot For
Untested 20wt% Cs/MoS₂

FIGURE 80. BET Plot for
Tested 20 wt% Cs/MoS₂

The surface area of the 20 wt% CsOOCH/MoS₂ before catalytic testing, but after drying to 300°C, was found to be 14 m²/g. This is also consistent with 13 m²/g reported previously [11]. The surface area of the Cs-doped catalyst after testing decreased to 6 m²/g. This decrease in surface area occurred over 551 hr of high temperature and high pressure conditions. Although a slight decrease in surface area to ≈11 m²/g during catalyst testing was previously reported [65], the loss of surface area for the present catalyst was quite significant. One possible reason for this loss of surface area is that the cesium formate could have agglomerated on the surface during testing. This agglomeration, in turn, could have blocked the pores of the catalyst, thus giving a lower surface area. This agglomeration may have been more pronounced in this catalyst, because a different doping method was used. Previously, the doping was carried out in vacuum [11]. For the current catalyst, doping was done at atmospheric pressure in air. This latter procedure might not allow the cesium to disperse into the pores. In this case of lower dispersion, under reaction conditions the cesium component could have more easily agglomerated.

Higher Surface Area Catalysts. Two higher surface area catalysts were produced, one with a surface area of 96 m²/g and another with 91 m²/g. The synthesized MoS₃ used to produce these catalysts was the same as for the previous catalyst. For the 96 m²/g MoS₂, approximately 2 g of MoS₃ was added with Pyrex beads to a quartz tube. The sample was flushed with nitrogen and then heated under nitrogen up to 210°C. This temperature was held for 10 min, and then the sample was heated up to 450°C at a rate of 13°C/min. This temperature was maintained for 1.5 hr. The sample was allowed to cool to room temperature under nitrogen, and then the sample was transferred from the quartz tube in air.

To obtain the MoS_2 with a surface area of $91 \text{ m}^2/\text{g}$, approximately 2 g of MoS_3 was added with Pyrex beads to the quartz decomposition tube. Under nitrogen flow, the sample was heated to 250°C and held there for 15 min. The sample was then heated at a rate of $15^\circ\text{C}/\text{min}$ up to 460°C , and this temperature was maintained for 2 hr. The sample was allowed to cool to room temperature under nitrogen. The sample was transferred from the quartz tube to a sample vial in air.

The surface areas of these two samples were determined as described previously. The BET plots obtained with these samples are shown in Figures 81 and 82, and a linear relationship was again observed.

FIGURE 81. BET Plot for
For 96 m²/g MoS₂

FIGURE 82. BET Plot
For 91 m²/g MoS₂

CONCLUSIONS

Computational studies were carried out in terms of the thermodynamic stability, the electronic structure, and redox properties of the sulfides of the transition metals in the early part of the periodic table. These analyses indicated that WS_2 , ReS_2 , and RuS_2 , as well as MoS_2 , should be stable catalysts under higher alcohol synthesis conditions. Thus, additional investigations should be carried out with these transition metal sulfides after surface doping with alkali metal cations, such as potassium and cesium.

It was shown that CsOOCH-doped MoS_2 catalysts can be reproducibly prepared and that reproducible catalytic behavior is observed with these materials. However, it was also shown that prolonged air exposure of the synthesized catalysts causes agglomeration of the CsOOCH dopant, leading to lower catalytic activity for the catalysts. Therefore, it is necessary to utilize freshly prepared catalysts protected from exposure to ambient air to obtain high alcohol synthesis activity Cs/ MoS_2 catalysts. For example, with a fresh 10 wt% CsOOCH/ MoS_2 catalyst, 300 g of linear alcohols/kg catal/hr were obtained from $\text{H}_2/\text{CO} = 1$ synthesis gas at 295°C, 8.3 MPa, and with GHSV = 7760 $\ell/\text{kg catal/hr}$. Under our reaction conditions, the presence of H_2S in the synthesis gas was not necessary to obtain stable activity, but the presence of 45.5 ppm of H_2S in the synthesis gas did tend to decrease the space time yield of methane, especially at the higher reaction temperatures.

The new preparation procedures explored for doping the MoS_2 catalysts did not result in improved catalysts, and the optimum alkali content of the catalysts is still very high, i.e. 10-20 wt% CsOOCH. New preparation techniques need to be developed to improve the alkali dispersion on the catalysts so that the number of active sites is increased while decreasing the content of promoter needed.

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