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 MoS_2 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°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% H_2S/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 $H_{0.22}MoS_2$ 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 $H_{0.1}MoS_2$ 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% H_2S/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% H_2S/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 MoS_2 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 H_2 occurred as a broad peak centered at 247°C. At 180°C, increasing the pressure of H_2 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_xMoS_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

[a] Blank (before H_2 adsorption)

der Waals gap. These samples were also studied using ^{1}H 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 MoS_2. Preparations of this catalyst included synthesizing two batches of MoS_3 under identical conditions. In a hood, 108 ml portions of 20% aqueous $(NH_4)_2S$ were added to 15.1520 g **(Batch 1)** or 15.0887 g **(Batch 2)** of $(NH_4)_2Mo_7O_{24} \cdot H_2O$ 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 $(NH_4)_2Mo_7O_{24} \cdot 4H_2O$ 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 $(NH_4)_2Mo_7O_{24} \cdot 4H_2O$ and $(NH_4)_2S$ 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 MoS_3 was prepared **(Batch 3)** using 15 g $(NH_4)_2Mo_7O_{24} \cdot 4H_2O$ and 106 ml of 22% aqueous $(NH_4)_2S$. The MoS_3 was washed with distilled water and dried overnight in air at 120°C.

Samples of $\mathbf{MoS_2}$ were prepared by calcination of MoS_3 under the flow of various gases. In each case, several 2-3 g portions of MoS_3 were calcined and then the portions were combined to form a larger batch of MoS_2. Gases utilized during the calcination treatment were:

1. Helium: **Catalyst Treatment A.** For this treatment, 2-3 g portions of MoS_3 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/MoS_3 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. H_2S/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% $CsOOCH/MoS_2$ 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

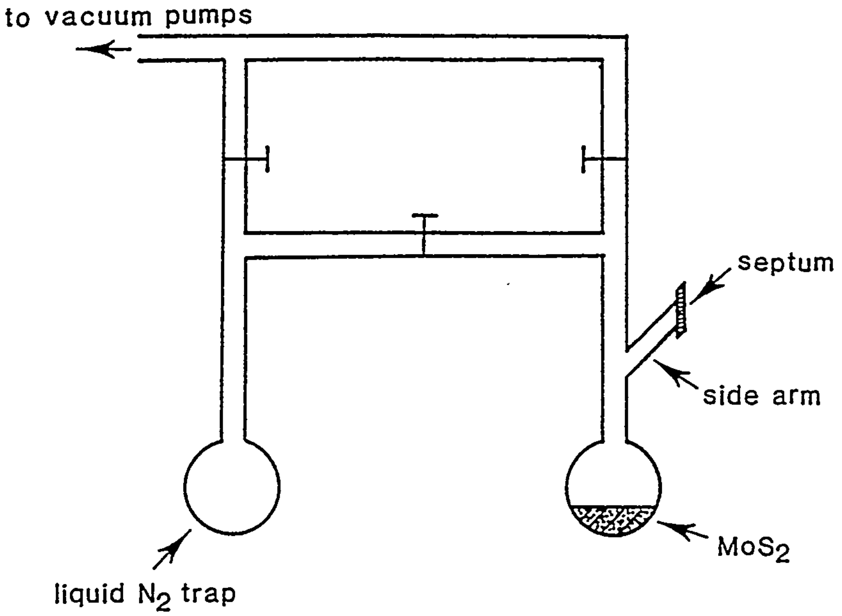

FIGURE 12. Diagram of the vacuum apparatus used in the preparation of alkali-doped MoS_2 catalysts.

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.

<u>10 wt% CsOOCH/MoS_2 Catalyst-Sample 2</u>. Another 10 wt% CsOOCH/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 (≈20°C/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 mol 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.

CsOOCH/MoS_2 = 13/87 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 ≈9 wt% Cs/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 $MoS_{2.00}$ (Batch 1, Sample A) and 12.89 wt% CsOOCH/$MoS_{1.92}$.

CsOOCH/MoS_2 = 20/80 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** MoS_2 and of the freshly prepared $CsOOCH/MoS_2$ catalyst.

Sample	Cs	Mo	S
MoS_2 (1B)	---	57.34	38.33
Cs/MoS_2	9.63	50.26	32.28

[a] Analyses carried out by Galbraith Laboratories

K/MoS_2 = 12.5/87.5 wt% Catalyst. The preparation procedure employed with this catalyst aimed at preparing MoS_2 containing intercalated potassium. Approximately 4 g of MoS_3 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 horizonal tubular furnace and a flow of N_2 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 N_2 flow.

A 1.7191 g portion of the MoS_2 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

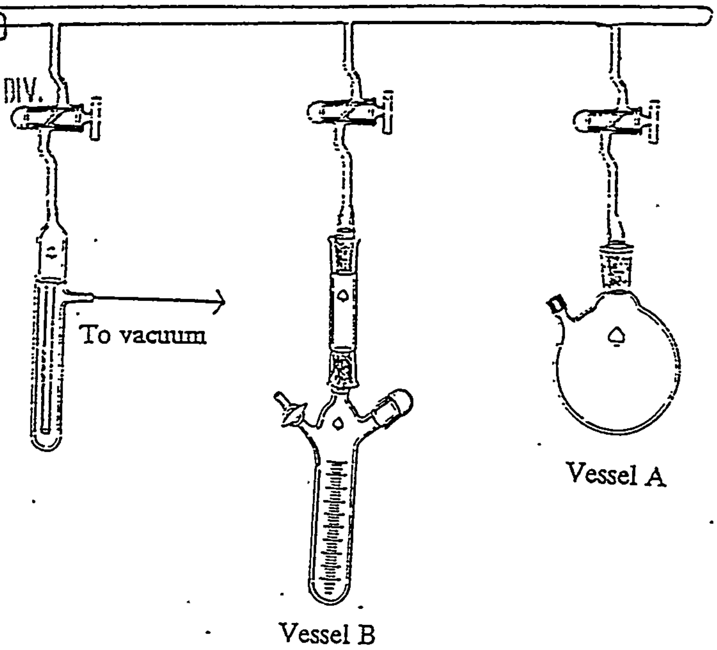

FIGURE 13. Apparatus used to prepare MoS_2 catalysts intercalated with potassium.

(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/MoS_2 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 MoS_2-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 MoS_2-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% 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% H_2/98 vol% N_2 with a rate of 60 ml/min for 1 hr in order

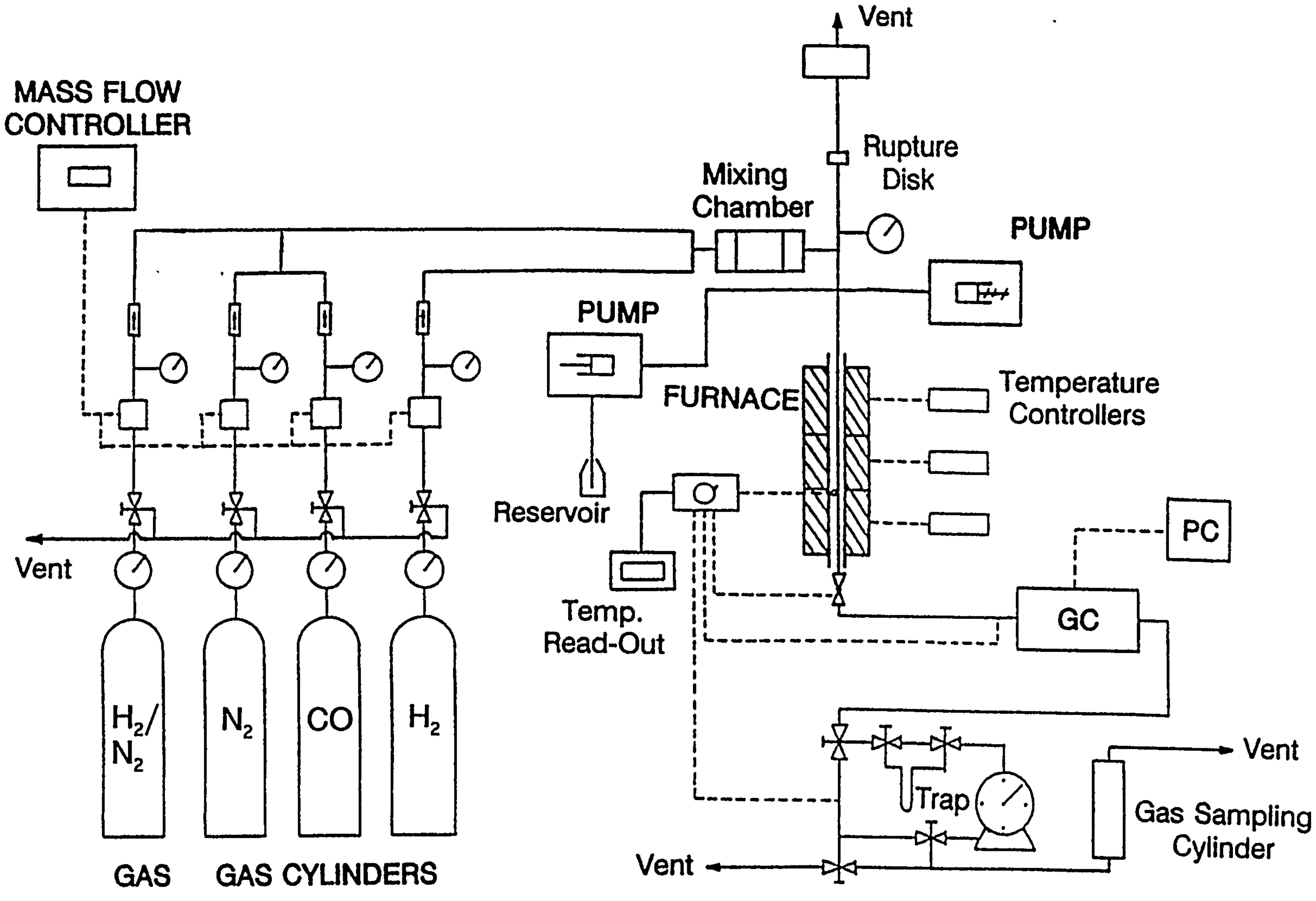

FIGURE 14. Schematic diagram of the alcohol synthesis reactor system used to test the undoped and alkali-doped MoS_2 catalysts.

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 proporties 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_{ii}, ζ_i and c_i 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.