MOLYBDENUM HEXACARBONYL AS A CATALYST PRECURSOR FOR DIRECT COAL LIQUEFACTION

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INTRODUCTION

Various transition metal carbonyls of the formula $M_x(CO)_y$ - where M is Cr, Fe, Co, Ni, Mo, Ru, Rh, W, Re - have been used effectively as catalyst precursors in laboratory-scale investigations of direct coal liquefaction (1-6). Most notable are the use of iron pentacarbonyl (4) and molybdenum hexacarbonyl (5). In particular, $Mo(CO)_6$ in the presence of sulfur has been shown to be an excellent catalyst precursor for the liquefaction of coal (5,6) and for promoting reactions with coal model compounds (7).

At PETC, $Mo(CO)_6$ has been used to study the influence of a catalyst on the liquefaction of coal (5,8,9). The inherent volatility of $Mo(CO)_6$ permits it to form an active liquefaction catalyst in the presence of sulfur with no special preparation, impregnation, or dispersion techniques. The liquefaction of coal is effectively accomplished by the simple direct addition of $Mo(CO)_6$ to the liquefaction reactor even in the absence of any added solvents or vehicles. The work reported here describes the activation and reactivity of the catalysts formed from $Mo(CO)_6$.

EXPERIMENTAL

The $Mo(CO)_6$ was used as received from Strem Chemical Company. Purity was given as 98+% with moisture being the only major contaminant. Ammonium tetrathiomolybdate (ATM) was purchased from Alfa Products and used as received. Elemental analysis of the ATM showed that it contained some oxygen; however, the S:Mo ratio was 4:1. In all of the experiments with coal, DECS-17 coal from the Penn State Coal Sample Bank was used. The coal was minus-60 mesh and was riffled prior to use. The elemental analysis (on a dry basis) provided with the coal was as follows: 76.3% carbon, 5.8% hydrogen, 1.3% nitrogen, 0.4% sulfur, 6.6% ash, and 9.7% oxygen (by difference).

Microautoclave experiments were performed according to previously described procedures (5,8,9). When $Mo(CO)_6$ was used with coal, no special impregnation or mixing procedures were used; it was simply added directly to the microautoclave containing the coal sample. Unless otherwise indicated, all of the experiments were conducted for 1 hour using a slow heat-up and rapid cool-down. The products were recovered according to the referenced procedures (5,8,9). Elemental analyses of the products were performed at Huffman Laboratories in Golden, Colorado. ESCA and X-ray diffraction analyses were performed at PETC.

RESULTS AND DISCUSSION

Conversion of $Mo(CO)_6$ to an Active Catalyst. $Mo(CO)_6$ is a sublimable solid that decomposes without melting at 150°C (10). In the absence of a liquid phase, the reactions involved in the transformation of $Mo(CO)_6$ to MoS_2 appear to take place in the gas phase as the carbonyl sublimes and decomposes. We have observed the conversion of $Mo(CO)_6$ in H_2S to MoS_2 in a high-pressure, windowed view cell. A description of the view-cell system has been published (8). In this experiment, 0.37 mmol of $Mo(CO)_6$ and 4.4 mmol of H_2S were added to the cell. At 90°C and 7.0 MPa, a brown coating started to cover the $Mo(CO)_6$ particles and the interior surface of the glass window. At 110°C the coating on the window prevented further visual observation. Inspection of the brown, mirrorlike coating on the window by XPS indicated that it was similar in composition to MoS_2.

To determine the fate of $Mo(CO)_6$ in our microautoclave liquefaction system, experiments were performed at several temperatures with $Mo(CO)_6$ and the results compared to those obtained from similar experiments with ATM, a nonvolatile liquefaction catalyst precursor. In these experiments, 0.9 g of the catalyst precursor and 9.1 MPa of a hydrogen/10% hydrogen sulfide gas mixture were charged to the microautoclave. The products from reactions with $Mo(CO)_6$ and ATM were recovered as methylene chloride-insoluble and tetrahydrofuran (THF)-insoluble residues, respectively. The S:Mo atomic ratios of the products determined from both elemental analysis and ESCA are contained in Table 1 along with the complete elemental composition.

Table 1. Activation of $Mo(CO)_6$

		Atomic S/Mo Ratio		Elemental
Temperature, °C	Precursor	Elemental	ESCA	Composition
175	$Mo(CO)_6$	2.5	---	---
250	$Mo(CO)_6$	2.0	1.3	$MoS_2C_{0.3}H_{1.7}O_{1.1}N_{0.1}$
250	ATM	2.3	1.8	$MoS_{2.3}C_{0.3}H_{2.4}O_{2.3}N_{0.3}$
375	$Mo(CO)_6$	2.3	1.8	$MoS_{2.3}C_{0.3}H_{0.9}O_{0.3}$
375	ATM	2.3	1.9	$MoS_{2.3}C_{0.3}H_{2.7}O_{1.8}N_{0.1}$

At 175°C, the lowest temperature investigated, approximately 45% of the carbonyl reacted to form a product with a S:Mo ratio of 2.5. Unreacted $Mo(CO)_6$ was also observed. An experiment with ATM was not performed under these conditions. At 250°C, no unreacted $Mo(CO)_6$ was observed. At this temperature, 97% of the carbon monoxide in the carbonyl was detected in the product gas. The products formed from $Mo(CO)_6$ and ATM at 250°C have slightly different S:Mo ratios. However, at 375°C, the products were similar in composition and close to the expected value of 2:1 for MoS_2. ESCA analyses of the samples indicated a lower S:Mo ratio on the surface, which was probably due to surface oxidation of the samples. Direct oxygen analyses of these samples confirmed the presence of oxygen.

X-ray diffraction analysis was also performed at PETC to determine the degree of crystallinity of the products from $Mo(CO)_6$ and ATM. At 175°C and 250°C, the products were essentially amorphous compounds; however, at 375°C the development of some crystallinity was observed.

Similar work on the transformation of $Mo(CO)_6$ and ATM under liquefaction conditions was reported by Artok et al. (6). Results with ATM are in agreement with those in Table 1; however, they reported lower S:Mo ratios (1.1 to 1.7) when using $Mo(CO)_6$. One possible reason may be that in our experiments, the H_2S:Mo ratio in the microautoclave system was initially about 6.3:1; whereas, in the work by Artok et al. it was reported as 2.5:1. Under typical coal liquefaction conditions in our system, at 1000 ppm Mo, the H_2S:Mo ratio was initially about 150:1.

The pressure and temperature data collected during microautoclave experiments were used to follow the change in the total number of moles of gas in the system with time. This provided information concerning the transformation of $Mo(CO)_6$ to an active catalyst and the temperature of the onset of catalytic activity. Determining the amount of gas in the system, especially during the heat-up period, from the pressure and temperature data was complicated by the fact that a significant portion of the reaction space is outside the heated sandbath. This cooler region consists of the internal volumes of the pressure transducer, connecting tubing, and associated valves. During heat-up and reaction, the gas in the cooler region would be at a higher density than the gas in the microautoclave. Therefore, calculating the moles of gas in the microautoclave system using the ideal gas law would result in an apparent decrease in the moles of gas as temperature increases.

An empirical correction procedure was developed that compensated for both the nonisothermal nature of the microautoclave system and the nonideality of the gas phase. This procedure involved determining a correction factor from pressure and temperature data from experiments with only H_2 or H_2/3% H_2S in the microautoclave system. This correction factor was obtained by fitting a polynomial equation to the apparent change in the moles of gas calculated using the ideal gas law as a function of the microautoclave temperature in these experiments. This correction factor was then applied to the moles of gas calculated using the ideal gas law from experiments with catalyst. This correction procedure is performed for each microautoclave reactor and is checked on a regular basis. Using this method, changes in gas content greater than $\pm$ 1 mmol can be reliably observed.

Figure 1 presents changes in the amount of gas present in the microautoclave system and the thermal history as functions of time for an experiment in which 3.7 mmol of $Mo(CO)_6$ was heated to 425°C under an initial pressure of 7.8 MPa H_2/10% H_2S. In section A of Figure 1, a rapid rise in amount of gas is first observed that starts at about 160°C as $Mo(CO)_6$ begins to decompose and liberate CO. This is close to the decomposition temperature of 150°C reported for $Mo(CO)_6$ (10). The amount of gas in the microautoclave continues to increase until, at 280°C, the trend reverses and a gradual decrease is observed. In another similar experiment, the reaction temperature was stabilized at 250°C for one hour after the heat-up period. After reaching 250°C, the gas content continued to increase smoothly to a level of 22 mmol and remained there for the duration of the experiment. This is equal to the maximum amount of CO that could have been liberated from the $Mo(CO)_6$ charged. Analysis of the gas composition by gas chromatography indicated that CO accounted for 95% of the carbon-containing gases produced.

To investigate the cause of the abrupt halt in the increase in gas content at 280°C and the onset of a gradual decrease, an experiment was terminated immediately upon reaching 325°C. Analysis of the recovered gases showed that some methanation and water/gas shift conversion had occurred, although carbon monoxide still accounted for 93% of the carbon-containing gases produced. The former reaction accounts for a reduction in the net moles of gas, while the latter gives evidence that water produced in the methanation undergoes catalytic reaction with CO.

In section B of Figure 1, a rapid decrease in the amount of gas occurs at temperatures above 350°C. This may be associated with an increased rate of methanation of the CO released from $Mo(CO)_6$. A fairly uniform rate of gas consumption (0.39 mmol/mmol Mo/min) occurred in the range of 370°C to 410°C.

At the end of one hour at 425°C the reaction was quenched (section C). Gas analysis indicated that all of the CO was utilized with 90% selectivity towards methane formation. The number of moles of gas present after quenching is lower than at the end of the reaction prior to quenching owing to the condensation of water vapor formed as a result of the methanation reaction. The amount of water indicated in Figure 1 (23 mmol) is in reasonable agreement with that expected based upon the amount of $Mo(CO)_6$ charged and the methane formed (20 mmol).

In Figure 2, the activation of $Mo(CO)_6$ in the H_2/10% H_2S environment is compared to similar experiments conducted in N_2 and H_2. The use of CS_2 as a source of sulfur in place of H_2S is also shown. In all four cases, the liberation of CO is observed. The largest and most uniform release of CO to the gas phase occurred when both H_2 and H_2S were present. In another experiment (not shown in Figure 2), the rate of release of CO was similar with N_2/10% H_2S to that observed with H_2/10% H_2S. The data in Figure 2 also show that the most active methanation catalyst was formed in the presence of just H_2. This is evidenced by the sharp decrease in gas content that occurred at 363°C. The rate of decrease in the temperature range of 380°C to 410°C was 0.55 mmol/mmol Mo/min. When N_2 was used, no significant drop in gas content occurred, either with (Figure 2) or without H_2S (not shown).

X-ray diffraction analyses of samples collected from the above experiments indicated that, in the presence of H_2/10% H_2S, the strongest peak was from MoS_2. The average crystallite size was 75 Å with a stacking height of 30 Å. The MoS_2-containing catalyst formed in the presence of N_2/10% H_2S had similar dimensions. When either N_2 or H_2 alone was used, the strongest peak was from Mo_2C. In these cases, the crystallites were more uniform in size with an average diameter of between 14 Å and 20 Å. Referring to the data in Figure 2, the carbide formed in the presence of H_2 appears to be a more reactive catalyst for methanation than the sulfided species. This agrees with published results obtained at 350°C and 101.3 KPa (11).

Effect of catalyst precursors on coal liquefaction. We have previously shown that $Mo(CO)_6$ is an effective catalyst precursor for coal liquefaction even in the absence of added liquids and special impregnation procedures (5,9). Compared with uncatalyzed reaction, the conversion of DECS-17 coal to primary (THF-soluble) products was facilitated over a wide temperature range by the catalyst formed from $Mo(CO)_6$. A different behavior was observed for the conversion of the primary to secondary (cyclohexane-soluble) products. In this case, the onset of catalytic conversion occurred between 375°C and 400°C.

Additional experiments were performed using the DECS-17 coal with various combinations of $Mo(CO)_6$, hydrogen, hydrogen sulfide, carbon disulfide, and nitrogen. When $Mo(CO)_6$ was used it was added at a level of 1000 ppm Mo based on daf coal. All of the experiments were performed at 425°C. The conversion results are shown in Figure 3. The error bars represent the range of values obtained about the average. The first set of data illustrates the high conversions obtained using $Mo(CO)_6$ with H_2/3% H_2S without added solvents or vehicles. The second and third sets of data show that a drop in both THF and cyclohexane conversions occurs if H_2S is eliminated; however, the conversions are still relatively high. Compared to no added sulfur (third set of data), using CS_2 appears to have no benefit. The fourth and fifth sets of data represent thermal conversions in the absence of catalyst. A small improvement is observed when H_2S is present, even in the absence of catalyst. Finally, the last two sets of data represent experiments performed in N_2. The presence of $Mo(CO)_6$ had no effect in the absence of H_2.

In the work with DECS-17 coal and $Mo(CO)_6$, it is assumed that $Mo(CO)_6$ sublimes and disperses onto the coal from the gas phase either prior to being sulfided or as it is converted to the sulfide phase. The previously described experiments in the view cell support this assumption. At the levels of Mo used in the experiments represented in Figure 3 (1000 ppm), the fate of the $Mo(CO)_6$ could not be determined using X-ray crystallography on the THF-insoluble residues owing to the small amount present and to interferences from the coal mineral matter in the residue. However, the residue from a similar experiment at 425°C in which $Mo(CO)_6$ was used at a higher level (10,000 ppm) could be examined if the mineral matter was first removed with hydrofluoric acid. In this case, X-ray diffraction analysis identified molybdenum disulfide in the THF insoluble product with a crystallite size of approximately 80 Å and a relatively low degree of stacking.

CONCLUSION

The results presented above confirm that $Mo(CO)_6$ forms a finely divided active catalyst for coal liquefaction even in the absence of added liquids or special impregnation procedures. Experiments with $Mo(CO)_6$ in an H_2/H_2S mixture show that the onset of hydrogenation activity related to methanation in the microautoclave system begins near 280°C and increases dramatically at about 350°C. Primary dissolution of coal assisted by the catalyst follows the same pattern; a small catalytic effect is observed at 325°C that increases in magnitude with temperature (5).

The decomposition of $Mo(CO)_6$ and the liquefaction of coal in the presence of this compound are both facilitated by the presence of H_2S. Substituting CS_2 for H_2S adversely affected $Mo(CO)_6$ decomposition and liquefaction conversion. In the absence of added sulfur, $Mo(CO)_6$ forms a carbide phase that is even a more active catalysts for methanation than the sulfide phase; however, this increased activity is not noted in liquefaction experiments with a low-sulfur coal. A different catalyst phase may be formed when coal is present.

The above work also demonstrates that with appropriate correction, the microautoclave pressure and temperature data can be used to follow changes in the amount of gas in the system during an experiment. Using this procedure, information on catalyst activation and reactivity were obtained. The same procedure has also been used to observe the influence of a catalyst on gas uptake during coal liquefaction (5).

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DISCLAIMER

Reference in this report to any specific product, process, or service is to facilitate understanding and does not imply its endorsement or favoring by the United States Department of Energy.

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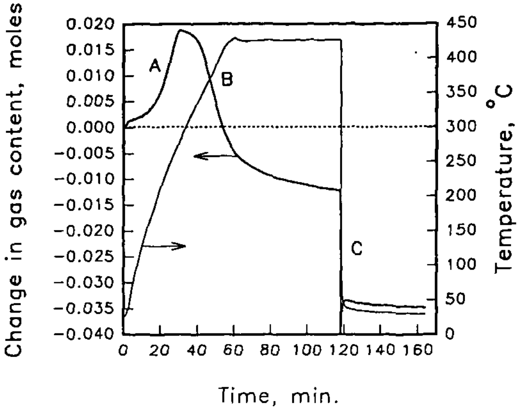

Figure 1. Reactivity of $Mo(CO)_6$in H_2/10% H_2S

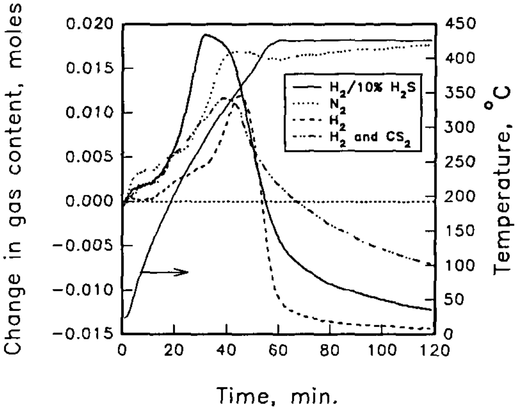

Figure 2. Reaction of $Mo(CO)_6$ in different systems.

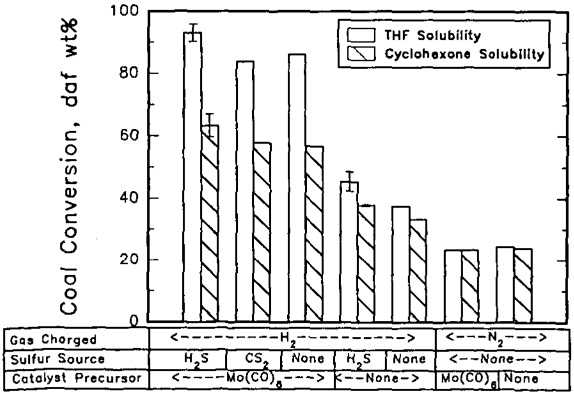

Figure 3. Effect of a catalyst, initial gas composition, and form of sulfur addition on the conversion of DECS−17 coal.