COMPARISON OF THE MEANS OF INTRODUCTION OF MoS_2 LIQUEFACTION CATALYSTS ON PERFORMANCE

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INTRODUCTION

The performance of dispersed coal liquefaction catalysts depends on many factors. One long recognized issue is the key importance of intimate contact between the catalyst and the reacting coal. The development of evidence for this critical relationship has been recently reviewed (1). The method of catalyst addition bears directly on this problem. For example, impregnation of coal with a catalyst precursor provides improved liquefaction conversion when compared to adding the precursor as a powder or as a particulate in a liquefaction solvent (2). Exploitation of the advantages obtained by impregnation of a catalyst or its precursors is still pursued.

Unlike most liquefaction catalyst precursors, $Mo(CO)_6$ has been found to be an effective catalyst precursor even in the absence of such impregnation procedures (3). The purpose of this paper is to compare the activity of the catalyst formed from $Mo(CO)_6$ with that of preformed MoS_2-containing catalysts known to be active for coal liquefaction. All of the liquefaction experiments were performed without the addition of liquefaction solvents or vehicles to avoid the leveling effect they may exert, especially if they are good hydrogen donors. The elimination of added solvents or vehicles also amplifies the importance of coal/catalyst contacting because mass transport becomes more restricted in reacting phases of higher viscosity.

EXPERIMENTAL

Coal and Chemicals: All experiments were performed with DECS-17 (Blind Canyon) coal (minus 60 mesh) from the Penn State Coal Sample Bank. 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 (0.02% pyritic sulfur), 6.6% ash, and 9.7% oxygen (by difference). The moisture content of the as-received coal was 3.7%. The coal was riffled prior to use. $Mo(CO)_6$ was obtained from Strem Chemical Company, ammonium heptamolybdate (AHM) was obtained from Fisher Chemical Company, and Panasol (a mixture of alkylated naphthalenes) was obtained from Crowley Chemical Company. All of the chemicals were used as received.

Catalyst Preparation: Three methods of introducing catalyst were used; addition of a catalyst precursor, recycle of the catalyst-containing residue from coal liquefaction experiments with the precursor, and addition of preformed catalyst particles. The catalyst precursor, $Mo(CO)_6$, was simply added directly to the microautoclave containing the coal sample without a special impregnation or mixing procedure. A MoS_2-containing liquefaction residue was prepared in a microautoclave using 6.6 g DECS-17 coal and $Mo(CO)_6$ (10,000 ppm Mo based on daf coal) under 7.2 MPa H_2/3% H_2S at 425°C for 1 h. Finely divided MoS_2-containing particles were prepared in a 1-L semi-batch stirred autoclave using 400 g Panasol and 10,000 ppm Mo (based on Panasol) as aqueous AHM (12% by weight) under 17.3 MPa, 30 mL/s H_2/3% H_2S at 400°C for 0.5 h (4). The MoS_2-containing particles and liquefaction residue were both recovered from tetrahydrofuran (THF) by pressure filtration following extraction of the respective reaction products. The dried liquefaction residue and MoS_2-containing particles contained 4.4% and 30% Mo, respectively.

Microautoclave Liquefaction Experiments: Microautoclave experiments were performed according to procedures described previously (3,5). The $Mo(CO)_6$, the liquefaction residue, or the MoS_2-containing particles were added directly to the microautoclave along with the coal (3.3 g) to give a Mo loading of 1,000 ppm (based on daf coal). No solvents or vehicles were used for catalyst addition or in the liquefaction experiments. All of the experiments were conducted for 1 hour at reaction temperatures from 350°C to 425°C under 7.2 MPa H_2/3% H_2S (cold pressure) using a slow heat-up and rapid cool-down. The products were recovered using sequential extractions with THF and cyclohexane according to the referenced procedures (3,5).

Catalyst Characterization: X-ray diffraction and BET surface area analyses were performed at PETC. A JOEL 200CX TEM located at the University of Pittsburgh was also used to obtain images of the MoS_2-containing particles. Additional details have been published (4).

The catalysts were also characterized by their activity for CH_4 production from CO in the absence of coal in the microautoclave under conditions similar to those used in the liquefaction experiments. In these experiments, either the liquefaction residue or the MoS_2-containing particles were added to the microautoclave at a level of approximately 0.4 mmol Mo. In the case of $Mo(CO)_6$, the MoS_2-containing catalyst phase was first formed in a separate experiment using 1.0 g of $Mo(CO)_6$ under 7.7 MPa H_2/10% H_2S and 1 h at 425°C (slow heat-up). A portion of the product sufficient to provide 0.4 mmol Mo was then added to the microautoclave. CO and a H_2/3% H_2S mixture were then combined in the microautoclave to give a gas mixture of approximately 75% H_2, 23% CO, and 2% H_2S at 7.7 MPa. Both slow and rapid heat-up experiments were performed at 375°C with a 1-h residence time at reaction temperature. The rates of gas uptake associated with the methanation reaction were obtained from records of the change in pressure with time. These data were used to calculate the change in moles of gas present in the system at reaction temperature.

RESULTS AND DISCUSSION

Microautoclave experiments were performed with Blind Canyon (DECS-17) coal to investigate the effect of the means of introducing catalysts on liquefaction. The catalyst was introduced either in the form of the chemical precursors $Mo(CO)_6$ and H_2S, or as MoS_2-containing compounds. Two MoS_2-containing compounds were used: (1) a liquefaction residue prepared from the precursors and the DECS-17 coal, and (2) high-surface-area MoS_2-containing particles prepared prior to the liquefaction experiments from AHM and Panasol.

We have previously shown that $Mo(CO)_6$ is an effective catalyst precursor for coal liquefaction even in the absence of added solvents or vehicles and special impregnation procedures (3). Table 1 contains the liquefaction conversion results from experiments using only the DECS-17 coal with and without 1000 ppm Mo added as $Mo(CO)_6$ in one-hour reactions at temperatures from 325°C to 425°C. All results are the average of at least two experiments. The influence of native catalyst precursors is negligible, owing to the low levels of pyrite in this coal.

Table 1. Liquefaction of DECS-17 coal using $Mo(CO)_6$ without added solvents or vehicles

Reaction Temperature, °C	THF Conversion, %		Cyclohexane Conversion, %	
	Thermal	Catalytic	Thermal	Catalytic
325	14	19	7	9
350	29	46	12	15
375	46	83	23	25
400	48	94	31	52
425	45	93	38	65

Compared to the uncatalyzed reaction, the conversion of coal to primary (THF-soluble) products was facilitated by the catalyst formed from $Mo(CO)_6$ even at the lowest temperature used, 325°C. The difference between catalytic and non-catalytic coal conversion continuously increased with temperature. In the case of secondary (cyclohexane-soluble) products, the onset of a significant catalytic effect occurred between 375°C and 400°C.

The observation of a catalytic effect at the lowest temperature used in the liquefaction experiments implies an active catalyst is formed at even lower temperatures. A detailed investigation of the activation of $Mo(CO)_6$ in the absence of coal under conditions similar to those used in the microautoclave liquefaction experiments has been reported (6). $Mo(CO)_6$ is a sublimable solid that decomposes without melting at 150°C (7). In microautoclave experiments, the evolution of CO associated with the decomposition was observed to begin at about this temperature. If H_2S was present, MoS_2 formed readily. When heated in an H_2/H_2S mixture, the development of catalytic activity was indicated by the conversion of the evolved CO to CH_4. The onset of catalytic methanation was detected near 280°C and increased dramatically at about 350°C. This result and the THF-conversion data shown in Table 1 confirm that an active catalyst is formed before significant thermal conversion of the coal begins.

A series of catalysts were formed in the microautoclave by heating $Mo(CO)_6$ in H_2/10% H_2S to various temperatures (6). The products were submitted to analysis by X-ray diffraction to determine the degree of crystallinity. At 175°C or 250°C, the products were essentially amorphous compounds. The development of some crystallinity was observed on raising the reaction temperature to 375°C. At 425°C, a higher degree of crystallinity was observed. The average crystallite size formed at this temperature was 75 Å with an average stacking height of 30 Å (~5 layers).

When the catalyst is formed in conjunction with coal, the $Mo(CO)_6$ apparently sublimes and disperses onto the coal from the gas phase either prior to being sulfided or as it is converted to the sulfide phase (6). At the levels of Mo used in the liquefaction experiments with $Mo(CO)_6$ (1000 ppm), it was not possible to determine the fate of the $Mo(CO)_6$ using X-ray crystallography on the THF-insoluble residues owing to the small amount of catalyst present and to interferences from the coal mineral matter which was concentrated in the residue. It was possible, however, to examine the MoS_2-containing liquefaction residue prepared from the DECS-17 coal and $Mo(CO)_6$ (see Experimental) by X-ray diffraction if the mineral matter was first removed by digestion with hydrofluoric acid. In this case, X-ray diffraction analysis identified MoS_2 in the THF insoluble residue with a crystallite size of approximately 80 Å and a relatively low degree of stacking as indicated by a very broad 002 line.

An alternative method for forming MoS_2-containing particles from AHM in Panasol has been reported (4). Elemental analysis of the MoS_2-containing particles was consistent with a composition of 50 wt% carbon and 50 wt% MoS_2 (4). X-ray diffraction showed that the MoS_2 was poorly crystalline. The average size in the basal plane was 25 Å. Absence of the 002 line implied the MoS_2 was essentially single layer. The dimensions obtained by X-ray diffraction were confirmed by TEM. The surface area of the particles determined by the BET method with nitrogen was 262 m^2/g.

To compare the three different means of introducing MoS_2, liquefaction experiments were carried out in the microautoclave using the DECS-17 coal at temperatures from 350°C to 425°C. All of the experiments were performed at least in duplicate. A comparison of the results for the two preformed catalysts with those obtained using $Mo(CO)_6$ (Table 1) was made by taking the difference between the conversion values for the catalysts. These differences are shown in Figure 1. The large error bars indicated on the zero line represent the range of conversion values obtained using $Mo(CO)_6$. The small error bars associated with the symbols for the two preformed catalysts represent the range of values obtained for these experiments. Error bars are not shown if they are smaller than the size of the symbol.

With respect to conversion to primary (THF-soluble) products, the data in Figure 1 show that the form of introduction of the catalyst has a significant effect on the primary dissolution and liquefaction of the coal. The catalyst formed in-situ from $Mo(CO)_6$ consistently yielded the highest conversions, especially at the lower temperatures. The MoS_2-containing particles were better than the MoS_2-containing liquefaction residue except at the lowest temperature where the conversions were similar. At 425°C, the MoS_2-containing particles did yield high levels of conversion similar to when $Mo(CO)_6$ was used.

A different picture emerges from Figure 1 regarding secondary conversion of the primary products to cyclohexane-soluble material. The form of introduction of the catalyst did not appear to have any significant effect at any temperature in this case.

The changes in the total number of moles of gas in the microautoclave system during experiments with and without the catalysts were determined from the pressure and temperature data collected during the experiments. A correction procedure was used to compensate for the nonisothermal nature of the microautoclave system and for nonideality in the gas phase (6). After subtracting the thermal results from the respective results obtained with the catalysts, plots of moles of gas versus reaction time show decreasing amounts of gas at all temperatures investigated. The onset of rapid hydrogen consumption differed for the different forms of catalyst. For $Mo(CO)_6$, the liquefaction residue, and the preformed particles, the onset of rapid hydrogen consumption occurred at approximately 370°C, 400°C, and 390°C, respectively. At 350°C, the rate of consumption for all catalysts was nearly constant for the entire reaction time at this temperature. At the higher temperatures, the rates of consumption were initially constant but decreased with time as the reaction proceeded.

The increment in coal conversion due to catalyst is plotted against values for the initial rates of gas uptake caused by catalyst in Figure 2. The increase in THF conversion attributed to catalyst correlates well with the initial rates of gas uptake when the uptake is plotted on a logarithmic scale. No such correlation is evident for conversion to cyclohexane soluble material.

MoS_2 is known to catalyze the hydrogenation of CO to form CH_4 (8). As an independent measure of catalyst activity, the rates of gas uptake associated with the conversion of a CO/H_2 mixture were obtained in the presence of the three forms of the catalyst. The preformed catalysts were simply added to the microautoclave as in the liquefaction experiments. For $Mo(CO)_6$, the catalyst species was first formed in a separate experiment without coal and a portion of this product was then used in the methanation test. Details are contained in the

Experimental section. Table 2 contains the rates of gas uptake observed using both slow and rapid heat-up to 375°C along with the respective conversions to THF-soluble products observed in the previously described liquefaction experiments at this same temperature (no rapid heat-up liquefaction experiments were performed).

Table 2. Comparison of methanation activity and liquefaction conversion at 375°C for different forms of MoS_2-containing catalysts.

Catalyst	Heat-up	Gas Uptake Rate (mmol gas/mmol Mo/min)	Liquefaction Conversion, daf wt%[1]
Mo-containing THF insols	slow	0.029	63
	rapid	0.041	--
MoS_2 Particles	slow	0.079	76
	rapid	0.085	--
Derived from $Mo(CO)_6$[2]	slow	0.032	83
	rapid	0.044	--

[1] THF conversions. The cyclohexane conversions were the same (25% to 26%) in all cases. [2] The methanation tests were performed with catalyst prepared in the absence of coal. The catalyst was formed in situ in the liquefaction tests.

The highest rate of gas uptake is that of the preformed MoS_2 particles derived from AHM and Panasol. The rates for the two materials derived from $Mo(CO)_6$ are lower and nearly the same whether the catalyst was formed with or without coal present. There is no direct correlation between the gas uptake rates observed for methanation and the values for coal conversion. A rationale for the different order of catalytic performance found for the gas-phase methanation and the coal liquefaction reactions may be more easily constructed when more data is in hand. For the present, it is worth noting that the experimental reactions are quite different with regard to rate restrictions that may be imposed by mass transport. Thus, coal/catalyst contacting may be a significant determining factor in the liquefaction experiments. The solvent-free character of these experiments accentuates the importance of mixing and contact with the reacting coal. For example, the most intimately mixed catalyst, that formed in situ from $Mo(CO)_6$, provides the highest coal conversion. When recovered in the liquefaction residue and recycled, conversion drops significantly. However, the activity determined by the gas-phase reaction for the liquefaction residue is not much less than observed for the catalyst made in the absence of coal. On the other hand, the particulate catalyst formed from AHM and Panasol shows higher activity for the gas-phase reaction, but does not perform as well as the more intimately mixed catalyst in the liquefaction experiment. The solvent-free liquefaction experiment reflects a combination of catalyst activity and coal contacting, while the gas-phase methanation test more nearly reflects a catalytic activity. It should also be borne in mind that the catalytic sites responsible for the two different reactions may not be the same. In view of the importance of establishing what factors limit the performance of dispersed catalysts, for example catalyst activity versus transport limitations, experiments now in progress are aimed at further exploring the relationship between methanation activity and liquefaction results.

CONCLUSION

The results show that the means of introduction of MoS_2-containing catalysts has a significant effect on the initial dissolution and conversion of coal to THF-soluble products, especially at temperatures below 425°C. The self-dispersing $Mo(CO)_6$ precursor provided the best conversions under the conditions of these experiments. More intimate contact between the catalyst and the reacting coal is thought possible in this case than with the preformed catalysts. Better contact could promote more hydrogen transfer from the gas phase to the reacting coal, preventing retrogressive reactions. The initial softening point of the DECS-17 coal is 385°C, and maximum fluidity is achieved at 420°C (Gieseler plastometer data provided with the coal). This increase in fluidity may be the reason performance of the different catalysts becomes more similar at the higher temperatures. Experiments with coals with different softening characteristics might be used to test this hypothesis.

On the other hand, the conversion of the coal to cyclohexane-soluble products was not affected by the form of introduction of the catalyst. This would imply that the reactions involved in forming these lighter materials occur at a point in the liquefaction process when all of the catalysts would be more uniformly distributed throughout the reaction mass.

Finally, the presence of coal appears to have an influence on the character of the catalyst formed from $Mo(CO)_6$. The X-ray data presented indicates that a reduced degree of stacking is observed for catalyst samples prepared in the presence of coal.

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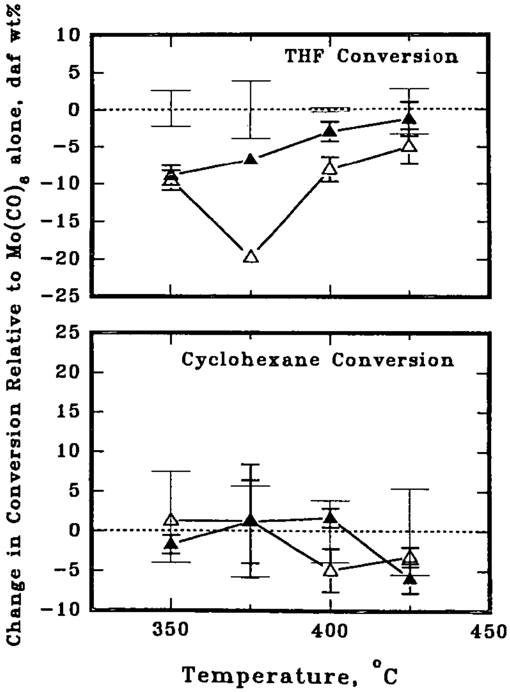

Figure 1. Effect of the means of introduction of catalyst on conversion of DECS-17 coal relative to direct addition of $Mo(CO)_6$. (△ MoS_2-containing liquefaction residue: ▲ preformed MoS_2-containing particles.)

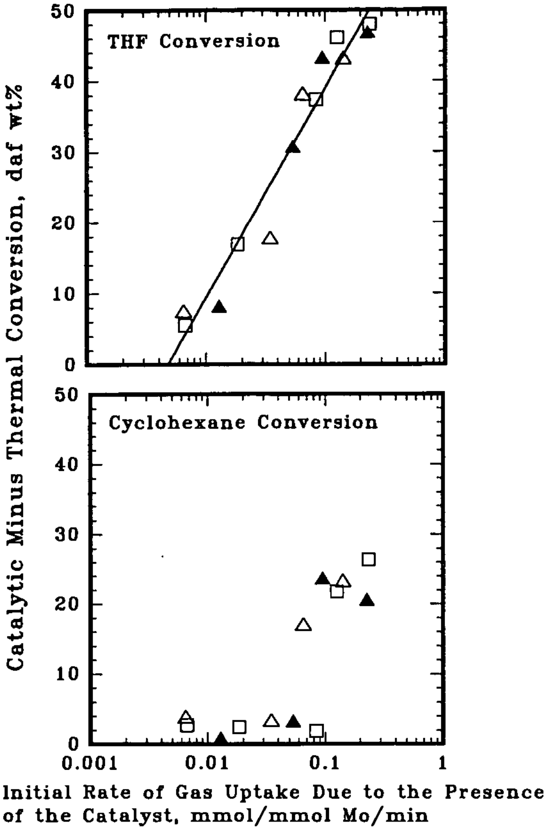

Figure 2. The dependence of catalyst-assisted conversion on the initial rate of gas uptake caused by the catalyst. (□ Mo(CO)$_2$; △ MoS$_2$-containing liquefaction residue; ▲ preformed MoS$_2$-containing particles.)