

# THE EFFECT OF CATALYST DISPERSION ON THE ACTIVITY OF UNSUPPORTED MOLYBDENUM CATALYSTS

Anthony V. Cugini, Donald V. Martello, Donald Krastman, John P. Baltrus, Michael V. Cicco, Elizabeth F. Frommell, and Gerald D. Holder\*

U.S. Department of Energy/PETC, P. O. Box 10940, Pittsburgh, PA, 15236 (\*University of Pittsburgh, Department of Chemical and Petroleum Engineering)

## INTRODUCTION

Unsupported catalysts have received considerable attention for coal liquefaction. These catalysts have been introduced into coal liquefaction systems by impregnation of the coal, as water-soluble salts, as volatile metal carbonyls, as oil-soluble organometallics, as finely divided powders, and as mineral matter associated with the coal and/or solvent.<sup>(1)</sup> For the most part, the method of catalyst precursor addition affected the observed catalyst performance. Weller et al.<sup>(2)</sup> found that, with ammonium heptamolybdate, coal impregnation resulted in higher coal conversions than physical mixing of the powder with coal. Others<sup>(3,4)</sup> have also observed this result. Additionally, Derbyshire et al.<sup>(4)</sup> found that the conditions used to dry the impregnated coal (removing the aqueous solvent used for solubilizing the catalyst precursor) affected the activity of the molybdenum. Joseph<sup>(5)</sup> and Artok et al.<sup>(6)</sup> reported that expanding the coal structure (by swelling during impregnation) improved the observed activity of the catalyst, possibly by allowing better contacting of the coal with the catalyst. Schlesinger et al.<sup>(7)</sup> found that results approaching those of impregnated MoS<sub>2</sub> could be obtained by thoroughly mixing a powdered catalyst with the coal using a ball-mill.

The results from the study of Schlesinger et al. suggests that it is difficult to determine if the mode of catalyst addition is important because of enhanced coal/catalyst contacting or if the mode of addition affects catalyst dispersion (i.e. the physical properties, surface area and/or particle size) of the ultimate catalyst. Other studies<sup>(8-11)</sup> have shown the importance of catalyst dispersion in determining the activity of unsupported molybdenum catalysts. Related work<sup>(12)</sup> demonstrated the importance of catalyst dispersion on iron catalyst activity.

The objective of this study was to decouple the coal/catalyst contacting and catalyst dispersion and to quantify the importance of both variables.

## EXPERIMENTAL

**Feedstocks:** The coals selected for use in this study had similar composition, but quite different particle sizes. Analyses of these coals, DECS-6 and DECS-17 Blind Canyon bituminous coals from the Department of Energy Coal Sample Base at Pennsylvania State University, are summarized in Table 1. Ammonium heptamolybdate (AHM), MoS<sub>2</sub>, ferric nitrate, and elemental sulfur were obtained from Fisher Chemical Co., tetrahydrofuran (THF), and ammonium tetrathiomolybdate (ATTM) from Aldrich Chemical Co. PANASOL<sup>®</sup>, a mixture of alkylated naphthalenes, was obtained from Crowley Chemical Co.

**Coal Impregnation:** Coal was impregnated with aqueous AHM using an incipient wetness technique. In the present study, 10 g of coal was wetted with an aqueous solution containing 6% by weight of molybdenum as AHM. After standing for 0.5 h, the water was removed from the wetted coal by vacuum drying at 40°C to a constant (10g) weight of coal. In some experiments where the coal was swelled during impregnation, the amount of solution necessary for incipient wetness was augmented by THF in the ratio of 9:1 THF to solution. The coal/catalyst solution/THF mixture was left to stand overnight and vacuum dried to remove the water and THF.

**Catalyst Penetration and Dispersion Measurements:** When coal is impregnated with a catalyst precursor, the precursor penetrates each coal particle to a limited extent. The depth of penetration into the coal particle was measured by two methods; X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy/scanning electron microscopy (EDS/SEM). A model LHS-10, Leybold XPS was used to determine the concentration of Mo on the surface of impregnated coal particles. The penetration of coal by the precursor was estimated by comparing the surface concentration with the overall Mo concentration impregnated into the coal. Measurements of the Mo penetration into the coal particles were made using an ETEC Autoscan Model U-1 SEM. The X-ray maps obtained from the SEM had an analytical spatial resolution on the order of 1 μm<sup>3</sup>. These measurements were a direct check of the Mo penetration obtained from the XPS examinations.

Catalyst dispersion was characterized by transmission electron microscopy (TEM), SEM,

X-ray diffraction (XRD), and BET surface area. A JEOL 200CX TEM was used to obtain images of MoS<sub>2</sub> crystallites. Similarly, SEM was used to obtain catalyst images and X-ray maps of a larger size range than those obtained by TEM. XRD analysis of the MoS<sub>2</sub> was performed using a Rigaku computer-controlled diffractometer to estimate MoS<sub>2</sub> crystallite size. The XRD size estimate was confirmed by TEM examinations of the same material. BET surface area was measured using a Coulter OMNISOORB 100 CX. Nitrogen adsorption was used for these measurements.

**Liquefaction Studies:** Experiments were conducted by adding 3.3 g of coal or impregnated coal to the 40-mL tubular microautoclave reactor with 6.6 g of PANASOL<sup>®</sup>. In experiments in which catalysts were used, 1000 ppm of Mo was added. The reactor was charged with the desired pressure of hydrogen and sealed. The pressurized reactor was then heated, either rapidly, 1-2 minutes, or slowly, 40 minutes, to the liquefaction temperature (425°C) in a fluidized sandbath. The liquefaction conditions were 425°C, 1000 psig H<sub>2</sub> (cold), added sulfur, and 0.5 h. Following the liquefaction period (0.5 h), the reactor was cooled and depressurized. Coal conversion was calculated from the solubility of the coal-derived products in tetrahydrofuran (THF) and in heptane as determined by a pressure filtration technique.<sup>(13)</sup>

**Catalyst Preparation:** Batches of powdered MoS<sub>2</sub>, for addition as a dispersed catalyst, were prepared in microautoclaves and 1-L autoclaves. The conditions used in these preparations were similar to the conditions used in the liquefaction studies. In the microautoclave, the precursor, aqueous AHM, powdered AHM, aqueous ATTM, or powdered MoS<sub>3</sub>, were added with PANASOL<sup>®</sup>. The conditions were 425°C, 1000 psig H<sub>2</sub> (cold), added sulfur, and 0.5 h (both slow and rapid heat-up of the reactor were tested). In the 1-L flow-through reactor the conditions used were 400 g PANASOL<sup>®</sup>, 10000 ppm Mo (based on PANASOL<sup>®</sup>) as aqueous AHM (12% by weight) or aqueous ATTM (3% by weight), 2,500 psig, 4 SCFH of H<sub>2</sub>/3% H<sub>2</sub>S, 400°C, and 0.5 h. In all cases the catalyst was recovered as the solids from a THF extraction of the reaction products.

## RESULTS:

**Catalyst Dispersion:** MoS<sub>2</sub> samples were prepared with different average particle and/or crystallite sizes and surface areas. The size and surface area were varied by using different precursor types, heat-up rates, and reactor types. The XRD-determined crystallite size and surface area for the different MoS<sub>2</sub> preparations are shown in Table 2. Introduction of the precursors as aqueous solutions appeared to give higher levels of dispersion than the powdered precursors. The 1-L stirred autoclave resulted in significantly higher dispersion than the shaken microautoclaves and aqueous AHM in the 1-L autoclave resulted in higher MoS<sub>2</sub> dispersion than aqueous ATTM (by BET surface area but not by XRD). The catalyst powder produced in the 1-L autoclave had an elemental composition of 50 wt% C and 50 wt% MoS<sub>2</sub>. SEM and TEM analysis qualitatively confirmed the relative levels of dispersion determined by BET and XRD. TEM examination of the MoS<sub>2</sub> produced from AHM and ATTM in the 1-L autoclave provided some explanation for the discrepancy in surface area and XRD crystallite size for the two catalysts. For the MoS<sub>2</sub> from AHM, the TEM analysis indicated that the particles were less than 25 Å (single layers) and were poorly crystalline. For the MoS<sub>2</sub> from ATTM, the TEM analysis indicated that the particles were small (perhaps less than 25 Å) but there appeared to be a longer range structure of the carbonaceous material associated with the MoS<sub>2</sub> that may have accounted for the lower surface area.

Liquefaction tests were made using the various MoS<sub>2</sub> samples with different levels of dispersion. The results are shown in Figure 1. The 0 m<sup>2</sup>/g surface area cases in Figure 1 represent data for no catalyst added. It appears that there is a linear relationship between catalyst surface area and conversion to THF and heptane soluble products. A similar trend was observed in plotting coal conversion with respect to inverse crystallite size (Figure 2). For the high surface area MoS<sub>2</sub>, the inverse crystallite size was calculated based on single layer MoS<sub>2</sub> with a stack height of 6 Å. These results indicate that at a constant level of addition of MoS<sub>2</sub>, the physical properties of the MoS<sub>2</sub> were very important in determining the ultimate activity observed. Note that for the one case of MoS<sub>2</sub> from ATTM in the 1-L autoclave, the activity was higher than predicted on the basis of surface area and lower than predicted on the basis of inverse crystallite size.

**Coal/Catalyst Contacting:** The DECS-6 and DECS-17 Blind Canyon coal were physically mixed with MoS<sub>2</sub>, impregnated with AHM by incipient wetness, or impregnated with AHM by incipient wetness with swelling (using THF) during impregnation. The effect of the method of catalyst addition on liquefaction activity is shown in Figure 3. The selection of powdered MoS<sub>2</sub> for the physically mixed comparison was made based on evaluation of the dispersion of MoS<sub>2</sub>

resulting from impregnation. The XRD analysis of MoS<sub>2</sub>, resulting from impregnated AHM treated at liquefaction conditions indicates a crystallite size of 46 Å thickness to 103 Å width (46/103Å). Swelling had little effect on this size (47/90Å). The physically mixed MoS<sub>2</sub> powder used for comparison had a crystallite size of 25/77Å. The results presented in Figure 3 indicate that the method of catalyst addition influences the ultimate observed activity. One explanation for the enhancement in activity observed with the impregnation techniques is that these techniques result in penetration of the coal particle by the catalyst precursor. The penetration depths of catalyst into the coal for these cases along with the physically mixed cases are shown in Table 3. Also shown in Table 3 is the fractional volume of coal that is also occupied by the catalyst (calculated from the penetration depth). It is apparent from this table that impregnation results in enhanced penetration of the coal particle by the catalyst. EDS/SEM analyses of these samples directly confirmed the relative penetration depths calculated from XPS data. Figures 4 and 5 present coal conversion as a function of penetration depth and fractional volume of coal occupied by the catalyst. The results indicate that the coal conversion is not so much a function of the penetration depth as it is a function of the fractional volume of coal occupied by catalyst, essentially a function of the extent of contacting between coal and catalyst. However the most significant difference in activity occurred between physical mixing and impregnation. Subtle differences (at most) were observed between the two modes of impregnation.

#### CONCLUSIONS:

The results of this study indicate that for catalysts with similar properties (size and surface area), the mode of catalyst addition affected the observed performance. Better catalyst performance was observed with impregnation than physical mixing. Also, for similar modes of catalyst addition, increasing the catalyst dispersion by decreasing the catalyst particle size (or increasing the surface area) results in higher observed activity. The results suggest that any comparison of catalysts should account for differences in catalyst dispersion and the mode of catalyst addition.

#### DISCLAIMER:

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

#### REFERENCES:

1. Derbyshire, F.J., Catalysis in Coal Liquefaction: New Directions for Research IEA CR/08 London, UK: IEA Coal Research, June 1988.
2. Chien, P.L., Chao, H., and Weller, S.W., *Ind. Eng. Chem. Proc. Des. Dev.*, **22**, pp 660-662 (1983).
3. Weller, S.W., *Proceedings: Fourth International Conference on the Chemistry and Uses of Molybdenum*, H.E. Barry and C.N. Mitchell, Ed., pp 179-186 (1989).
4. Derbyshire, F.J., Davis, A., Lin, R., Stansberry, P.G., and Terrer, M.T., *Fuel Processing Technology*, **12**, pp 127-141(1986).
5. Joseph, J., *Fuel*, **70**, pp 459-464 (1991).
6. Artok, L., Davis, A., Mitchell, G.D., and Schobert, H.H., *Fuel*, **71**, pp 981-991 (1992).
7. Schlesinger, M.D., Frank, L.V., and Hiteshue, R.W., Bureau of Mines Report No. 6021 (1961).
8. Frety, R., Breyesse, M., Lacroix, M., and Vrinat, M., *Bull. Soc. Chim. Bulg.*, **93**(8,9), pp 663-672 (1984).
9. Busetto, L., Ianibello, A., Pincolini, F., and Trifiro, F., *Bull. Soc. Chim. Bulg. Proc. Des. Dev.*, **90**(12), pp 1233-1248 (1981).
10. Ratnasamy, P. and Leonard, A.J., *Journal of Catalysis*, **26**, pp 352-358 (1972).
11. Utz, B.R., Cugini, A.V., and Frommell, E.A., Novel Materials in Heterogeneous Catalysis, Baker, R.T., and Murrell, L.L., Ed., ACS Symposium Series No. 437 Chapter 27 (1989).
12. Cugini, A.V., Krastman, D., Martello, D.V., Frommell, E.F., Wells, A.W., and Holder, G.D., *Energy & Fuels*, **8**(1), pp 83-87 (1994).
13. Utz, B.R., Narain, N.K., Appell, H.R., and Blaustein, B.D., Coal and Coal Products: Analytical Characterization Techniques, Fuller, Jr., E.L., Ed. ACS Symposium Series No. 205, p. 225 (1982).

Table 1. Analyses of Feed Coals

	Blind Canyon, DECS-6	Blind Canyon, DECS-17
<b>Proximate Analysis, wt% as received</b>		
Moisture	4.73	3.7
Volatile Matter	42.4	45.0
Fixed Carbon	47.3	44.9
Ash	5.6	6.3
<b>Ultimate Analysis, wt% moisture free</b>		
Carbon	76.5	76.2
Hydrogen	5.9	5.8
Nitrogen	1.5	1.3
Sulfur	0.4	0.4
Oxygen (Diff.)	9.9	9.6
Ash	5.8	6.8
<b>Sulfur Forms, wt%</b>		
Sulfate	0.01	0.01
Pyritic	0.02	0.02
Organic	0.37	0.41
<b>Average Particle Size, um</b>	397	84

Table 2. MoS<sub>2</sub> Physical Properties

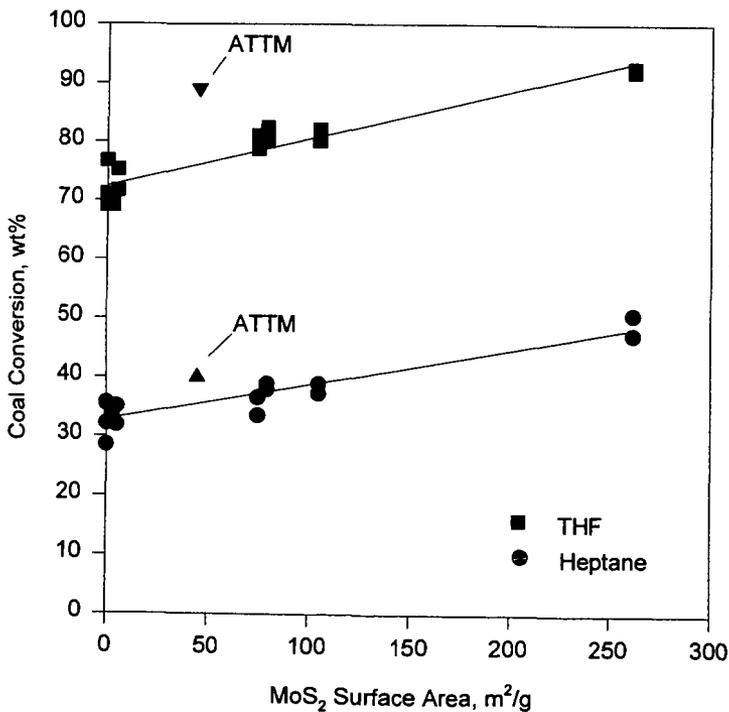
Precursor	Gas, Heat-up	Reactor Type	BET Surface Area, m <sup>2</sup> /g	XRD Crystallite Size, Å Height/Width
MoS <sub>2</sub>	na	na	2.7	very ordered
AHM, Powdered	H <sub>2</sub> /H <sub>2</sub> S slow	Microautoclave	na	very ordered
ATTM	H <sub>2</sub> fast	Microautoclave	79.5	26 / 78
ATTM	N <sub>2</sub> fast	Microautoclave	84.4	27 / 78
ATTM	H <sub>2</sub> slow	Microautoclave	74.9	30 / 81
MoS <sub>3</sub>	H <sub>2</sub> fast	Microautoclave	104.8	25 / 77
AHM (aq)	H <sub>2</sub> /H <sub>2</sub> S slow	Microautoclave	na	46 / 103
AHM (aq)	H <sub>2</sub> /H <sub>2</sub> S slow	1-L Autoclave	262.0	--* / 25
AHM (aq)	H <sub>2</sub> /H <sub>2</sub> S slow	1-L Autoclave	243.0	--* / 25
ATTM (aq)	H <sub>2</sub> /H <sub>2</sub> S slow	1-L Autoclave	45.0	--* / 25

\*001 line was not observed.

Table 3. Effect of Mode of Addition and Coal Particle Size on Penetration Depth and Percent of Coal Contacted.

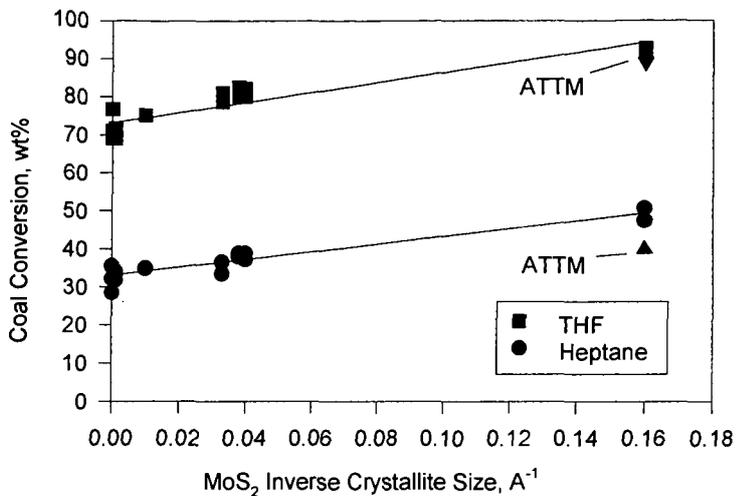
Particle Size, $\mu\text{m}$	Mode of Addition	Penetration Depth, $\mu\text{m}$	Percent of Coal Contacted, %
397	Physically Mixed	1	1.5
84	Physically Mixed	1	7.0
84	Aqueous Impregnation	4.7	29.7
397	Aqueous Impregnation	9.4	13.6
84	THF-Assisted Aqueous Impregnation	13.7	69.5
397	THF-Assisted Aqueous Impregnation	16.0	22.3

Figure 1. Effect of  $\text{MoS}_2$  Surface Area on Blind Canyon Coal Conversion



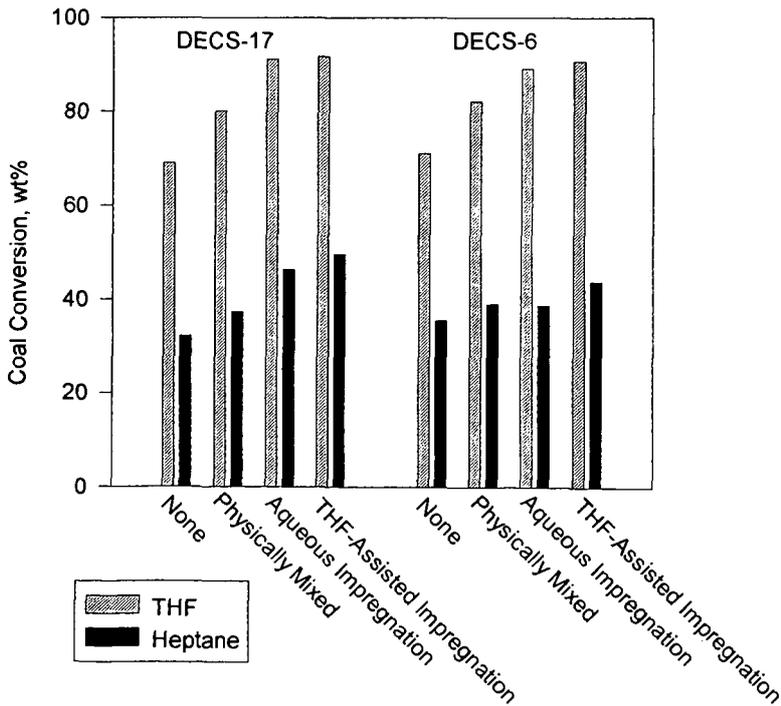
2:1 PANASOL to Coal, 425°C, 1000 ppm Mo, 1000 psig H<sub>2</sub> (cold) and 0.5 h

Figure 2. Effect of MoS<sub>2</sub> Inverse Crystallite Size on Blind Canyon Coal Conversion



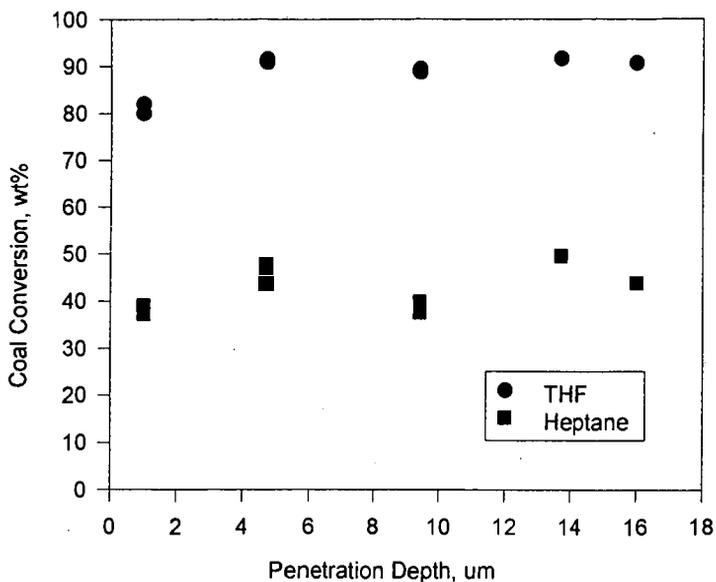
2:1 PANASOL to Coal, 425°C, 1000 ppm Mo, 1000 psig H<sub>2</sub> (cold), and 0.5 h

Figure 3. Effect of Method of Catalyst Addition



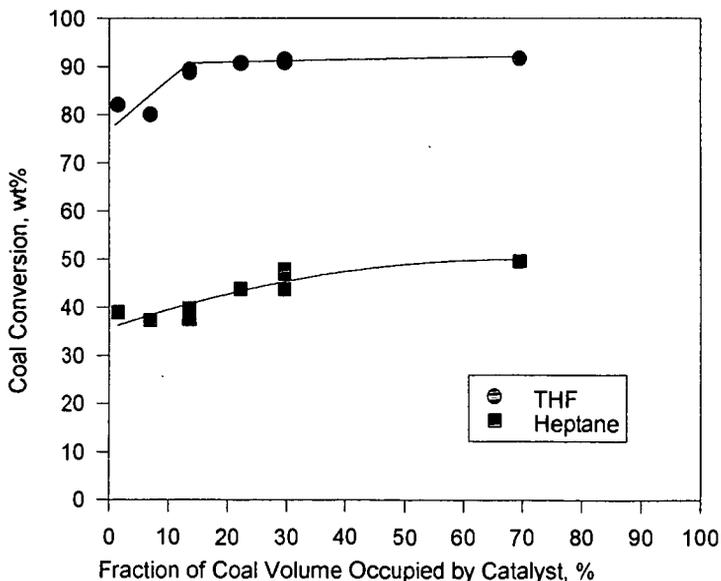
2:1 PANASOL to Coal, 425°C, 1000 ppm Mo, 1000 psig H<sub>2</sub> (cold), and 0.5 h

Figure 4. Effect of Penetration Depth on Blind Canyon Coal Conversion



2:1 PANASOL to Coal, 425°C, 1000 ppm Mo, 1000 psig H<sub>2</sub> (cold), and 0.5 h

Figure 5. Effect of Coal Contacted on Blind Canyon Coal Conversion



2:1 PANASOL to Coal, 425°C, 1000 ppm Mo, 1000 psig H<sub>2</sub> (cold), and 0.5 h