

CONVERSION OF OXO AND THIOMOLYBDATES TO ACTIVE DISPERSED CATALYSTS

Xiaodong Zhan, Mike Dieterle, Anthony Lucas
Howard Van Woert, and Edwin N. Givens

Center for Applied Energy Research
University of Kentucky
2540 Research Park Drive
Lexington, KY 40511-8410

Keywords: Molybdenum catalyst, Coal Liquefaction

ABSTRACT

Oxomolybdates impregnated on coal are excellent catalyst precursors in the liquefaction of Wyodak coal, especially when sulfur is added during the reaction. It has been suggested that the active catalysts are oxothiomolybdates. This paper discusses two approaches toward converting oxomolybdates into active catalysts and identifying the types of Mo-S bonding that contribute toward their activity. In the first, several oxothiomolybdates having different forms of Mo-S bonds were prepared in our laboratory and impregnated onto Wyodak coal. THF dissolution and resid conversion for these precursors were determined both in the presence and absence of added H_2S . In the second approach, ammonium heptamolybdate was treated in flowing H_2S in H_2 at temperatures to permit slow conversion of the oxomolybdate into its active form. The effect of this pretreatment on the activities of these catalyst impregnated coals were determined.

INTRODUCTION

A vast amount of observations has indicated that the presence of sulfur is important to coal liquefaction. For molybdenum based catalyst, it is generally agreed that the predominant active species for the primary coal liquefaction is some form of molybdenum sulfide, e.g., MoS_2 . The active species may be produced by the decomposition of molybdenum precursors under liquefaction condition. When metal sulfide catalysts are used, a source of sulfur such as hydrogen sulfide, carbon disulfide, or elemental sulfur is introduced to the reactor to maintain the catalysts in a sulfided form. If the precursor contains no sulfur, external sulfur participates in forming the highly active phase. If excess sulfur is present in a sulfur containing precursor, some must diffuse out to allow transformation into the active phase to occur.¹ The importance of the correct stoichiometry of Mo sulfide has also been emphasized by Montano.²

The type of catalyst precursor and its activation conditions are important factors influencing the function of the molybdenum catalyst. Utz et al.³ compared the effects of ammonium tetrathiomolybdate (ATTM), MoS_2 , and ammonium heptamolybdate (AHM) on the liquefaction yields of coals. Two activation methods employed were rapidly heating up the reactor to 450°C in 1-2 minutes and slowly heating up in 45-60 minutes. Their results showed greater activities of ATTM and MoS_2 when they were heated rapidly, while slow heating favored AHM. They suggested that since ATTM and MoS_2 were already in a sulfided form, they could decompose more rapidly to a highly dispersed active phase. The transition of AHM to MoS_2 having a high surface area was slow because an external sulfur source was required. By studying the temperature and pressure profiles in a batch reactor, Bockrath et al.⁴ found that the molybdenum sulfide was able to participate in liquefaction reactions at low temperature, e.g., 350°C, in contrast to the conventional 400-465°C. They concluded that the dispersed catalyst should be present in an already active form rather than allowing a precursor to undergo transformation during liquefaction. The influence of catalyst precursor on coal conversion also was investigated by Hirschon and Wilson,^{1,5} who used Illinois #6 coal with various molybdenum precursors. They found that much higher toluene solubles could be obtained with organometallic complexes than with aqueous metal salts. They suggested that the higher activity of the molybdenum sulfide complex could be attributed to its better dispersion and already being present in highly active form. Subsequent activation during liquefaction was unnecessary. Our recent studies indicate that low-cost water-soluble oxomolybdate salts can be transformed into liquefaction catalysts having activity comparable to more expensive oil soluble precursors.⁶

Although oxomolybdates have demonstrated substantial activity toward coal liquefaction in the presence of H_2S , we suspect that their transformation into active phase can be achieved in situ. The objective of this study is to investigate approaches for improving the activity of dispersed catalysts generated from oxomolybdates. A series of Mo based compounds with various sulfur content were prepared from H_2S and oxomolybdate before impregnating them on coal. Another approach that was also tested was to pretreat the oxomolybdate impregnated coal slurry with H_2S in H_2 to convert the precursor to oxothiomolybdate prior to reaction. This method has been reported to form an active catalyst or close intermediate to an active species.^{7,8}

EXPERIMENTAL

Materials Elemental analysis of the Black Thunder Wyodak coal are presented in Table 1. The as-received coal was impregnated with an aqueous solution containing various concentrations of catalyst precursors at the level of 0.5 g solution/g coal. The concentration of the aqueous solution was varied so that desired Mo loadings on coal could be achieved. In all of the cases, the coal paste was dried at 125 Torr and 100°C for two days to completely remove water. Solvent used in this study comprised mixtures of heavy distillate and deashed resid from Run 262e made at the Advanced Coal Liquefaction R&D Facilities at Wilsonville, AL. The properties of these materials, which were produced when the plant was operated with the same coal, are also summarized in Table 1. Ammonium heptamolybdate (AHM, Aldrich, A.C.S. reagent) and tetrahydrofuran (THF, Aldrich) were used as received. Ammonium dioxodithiomolybdate (ADOM), ammonium tetrathiomolybdate (ATTM), and three types of ammonium polythiomolybdate having different sulfur contents were prepared in our lab from AHM and H₂S. ATTM was prepared by the method of Naumann and Behan⁹, AOTM was prepared by the method of McDonald et al.,¹⁰ APTM-1A and APTM-2A ((NH₄)₂[Mo₂S₁₂]·2H₂O) were prepared by the method of Müller and Krickemeyer,¹¹ and APTM-P ((NH₄)₂Mo₃S(S₂)₆·2H₂O) was prepared by the method of Kurtak and Hartzog.¹² The compositions of these material are summarized in Table 2. In all experiments, catalyst loadings were reported as mg Mo per kg dry coal.

Catalyst Pretreatment In some of the experiment, the oxomolybdate impregnated coal slurry was pretreated prior to reaction with H₂ containing 8 vol% H₂S. In a typical run, the reactor was loaded with coal slurry and placed horizontally in a furnace after purging with H₂ to remove air. The pretreatment was conducted at 300 psig and a gas flowrate of 200 ml/min (STP). The furnace was heated to 120 °C and held for 30 min after which it was successively heated to 250 and 360 °C while holding for 30 minutes at each temperature. After pretreating at 360 °C, the reactor was cooled, vented and subjected to regular reaction procedures described in the following section.

Coal Liquefaction Reaction Procedures All of the experiments were conducted in a 65 ml microreactor which was agitated at 400 rpm in a fluidized sand bath (Technique, SBL-2D) maintained at 440°C with an Omega CN4600 temperature controller. In every run, 3 g dry coal, 1.8 g heavy distillate, and 3.6 g deashed resid were added to the reactor which was then pressurized to 1000 psig at room temperature with H₂ containing 3 vol% H₂S. Except in some runs when the reactor was charged with pure H₂ only, all reactions were performed at the above baseline reaction conditions. After 30 minutes reaction time, the reactor was removed and quenched in ice water. The liquid and solid products were scraped from the reactor using THF and subjected to Soxhlet extraction for 18 hours. The THF soluble material was distilled at 1 Torr and an atmospheric equivalent cut point of 566°C according to ASTM method D-1160. This cut point corresponds to that used in the pilot plant where the solvent was generated. All experiments were replicated at least twice to assure the reproducibility.

THF coal conversion and resid conversion were defined below as a measure of catalyst activity on an maf coal basis.

$$\text{Coal Conv.} = 100 \times \left(1 - \frac{[\text{IOM}]_{\text{product}}}{\text{Coal}(\text{maf})} \right) \quad (1)$$

$$\text{Resid Conv.} = 100 \times \left(\frac{[\text{Coal}(\text{maf}) + \text{Resid}]_{\text{feed}} - [\text{IOM} + \text{Resid}]_{\text{product}}}{\text{Coal}(\text{maf})} \right) \quad (2)$$

RESULTS AND DISCUSSION

Effect of Oxothiomolybdates on Coal Liquefaction In this study, several sulfur containing molybdenum compounds including AOTM, ATTM, and three types of APTM were used as catalyst precursors to examine the effect of sulfur content in precursors on liquefaction. Conversions with these precursors at Mo loading of both 100 and 300 ppm are shown in Figures 1 and 2.

In the presence of H₂S, coal conversion was almost unchanged at both catalyst loadings. However, in the absence of added H₂S, coal conversions increased significantly for precursors having S/Mo ratios ≥ 4. Another sizable increase was observed for APTM-1A which contains a S/Mo ratio of 10.9. This material had been extracted with CS₂ to remove free sulfur and probably contained a large fraction of polysulfide bonds. As shown in Figure 2, resid conversion increased slowly as the S/Mo ratio increased, whether in the presence or absence of H₂S. Because of the wide variations observed in the resid conversion values, however, the data do not show a statistically significant difference between precursors having S/Mo ratios from 2 to 6. Overall, the presence of sulfur is important to both coal and resid conversions whether sulfur is supplied externally or is present in the catalyst precursor. Lower conversions observed in the absence of H₂S may be due to insufficient sulfur in the reactor to sulfide the precursors and to protect the active phase from being oxidized by

the water. Since the fraction of converted precursor apparently increased as sulfur increased, coal conversion also increased as the S/Mo ratio in the precursor increased. When H₂S was introduced to the reactor, the amount of sulfur carried in by the precursor became negligible compared to the total sulfur available, thus coal conversion became independent of the S/Mo ratio.

Since coal solubilization takes place very early during liquefaction, without added H₂S, the small amount of sulfur associated with the precursors may be sufficient to transform and stabilize an active phase for a short period. Within that period when conversion is occurring, THF solubilization showed an increase as the S/Mo ratio in the precursor increased. Since resid conversion progresses over a longer period, the active phase may lose sulfur through oxidation by water causing the catalyst to deactivate. Thus, an added source of sulfur is necessary to maintain the catalyst in an active form. Clearly, an external sulfur source is necessary for precursors already containing a significant concentration of sulfur.

In coal liquefaction with impregnated catalyst, it is generally assumed that catalyst precursor converts to sulfided active phase *in situ*. There is evidence showing that the activity of the final catalyst depends upon the conditions employed during its preparation.⁷ At high temperatures typical of coal liquefaction, an oxomolybdate catalyst precursor such as AHM experiences two type of competition reactions, i.e., thiosubstitution and decomposition. When the rate of ammonia loss due to decomposition is greater than the rate of thiosubstitution, the intermediate Mo compounds are more difficult to sulfide. Therefore, complete sulfidation of ammonium oxomolybdate by H₂S under liquefaction conditions may not occur. By contrast, in oxothiomolybdates, the loss of ammonia is not critical since the catalysts are already in their sulfided forms. Complete conversion of these precursors to an active catalyst is more likely through reaction with the H₂S or intramolecular rearrangement transfer of the sulfur in precursors. For different sulfur-containing precursors, there may be differences in their decomposition mechanisms and kinetics. The chemical form and the number of active sites may also differ as reflected by the different activities towards resid conversion.

Another factor that affects the formation of active catalyst is the presence of water. Although the impregnated coal was dried before reaction, inevitably, some water will be present in the reactor as a result of deoxygenation reactions. At high temperatures and in the presence of water, the Mo catalyst will deactivate as it gains oxygen from water. Also, water may cause removal of sulfur, thus deactivating the catalyst. The observation that resid conversion increases with the S/Mo ratio in the presence of H₂S may also be attributed to the fact that the oxothiomolybdate catalyst may remain the active phase as excess sulfur is lost in the presence of water.

Pretreatment of oxomolybdate impregnated coal slurry with H₂S/H₂ Sulfur is obviously important for the transformation of these oxo and thiomolybdate precursors into an active catalytic phase. In order to have a better understanding of this transformation, a series of tests were made in which AHM impregnated coal slurries were pretreated with H₂S. In every run, the catalyst impregnated coal was dried, slurried with solvent, and pretreated in a stream of H₂S/H₂ at a series of temperatures at 300 psig.

A blank run was made to determine the effect that pretreating coal for 90 minutes at a sequence of temperatures up to 360°C would have on conversions at 440°C. THF and resid conversions for a coal impregnated with AHM to a Mo loading of 100 ppm were quite small, i.e., 3.6% and 2.4%, respectively. Therefore, conversions observed at 440 °C are not significantly influenced by the 90 minutes pretreatments at ≤ 360°C and 300 psig.

For coals impregnated with 100 and 300 ppm Mo, THF coal conversions were not affected by the pretreatment, as shown in Figure 3. The most noticeable effect is an increase in resid conversion for the coal loaded with 100 ppm Mo. The resulting resid conversion is the same as that achieved with the coal loaded with 300 ppm Mo. This result suggests that the pretreatment converts a large fraction of the precursor to an active phase. At the 300 ppm Mo loading, no apparent advantage was gained from pretreating.

It appears that pretreating the coal slurry with H₂S/H₂ improves resid conversion. Also, high resid conversions can be obtained by using an oversulfided Mo substrate such as APTM-1A. Note that the following two 100 ppm Mo impregnated coals were as active as the 300 ppm Mo impregnated coals.

	Resid Conv, maf coal
100 ppm Mo as AHM+treatment with H ₂ S/H ₂	82.3±1.7
100 ppm Mo as APTM-1A	82.3±2.9
300 ppm Mo as AHM+treatment with H ₂ S/H ₂	82.2±1.6
300 ppm Mo as AHM	80.3±0.4

CONCLUSIONS

When non-sulfur containing oxomolybdate was used as catalyst precursor for coal liquefaction, complete transformation to active catalyst *in situ* apparently does not occur under

reaction conditions. Upon recycle, the Mo-catalysts have been observed to be far more active. The inevitable presence of water in the reaction system at the high reaction temperature affects this transformation. If oxothiomybdate is used as precursor or if oxomybdate impregnated coal is presulfided prior to reaction, activity for resid conversion improves substantially and is retained for a longer period. In these cases, the catalyst is more active and more resistant to water oxidation. An external sulfur is still necessary with oxothiomybdate precursors.

ACKNOWLEDGMENTS

This research project was supported by the U.S. Department of Energy under contract number of DE-AC22-91PC91040.

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	Coal	Solvent	
	Ultimate Analysis	Heavy Distillate	Deashed Resid
<566°C	-	96.9	14.7
Composition (wt%)			
Carbon	70.62	88.86	89.79
Hydrogen	5.03	9.91	7.26
Nitrogen	1.13	0.44	0.86
Sulfur	0.52	<0.03	0.03
Oxygen (diff)	16.38	0.79	1.33
Ash	6.32		0.73
Ash, SO ₃ -free	5.46		

	AHM	AOTM	ATTM	APTM-P	APTM-2A	APTM-1A
H	2.59	3.58	3.08	1.30		1.16
N	6.80	11.7	10.77	3.76		3.0
S	0	28.28	49.23	55.05	60.23	72.16
Mo	54.37	43.97	36.92	36.76	31.05	19.91
O (diff)	36.24	12.47	-	3.13		3.77
S/Mo (atomic)	-	1.93	4.00	4.49	5.82	10.87

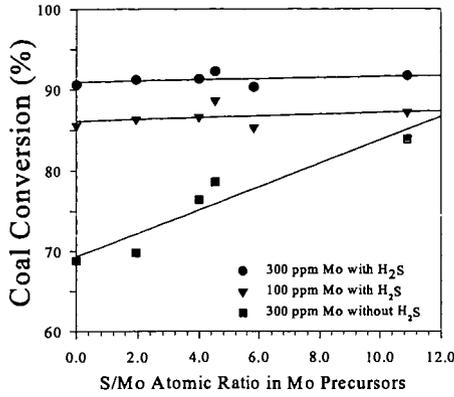


Figure 1. Effect of S/Mo ratio in precursors on coal conversion in the presence/absence of external H₂S

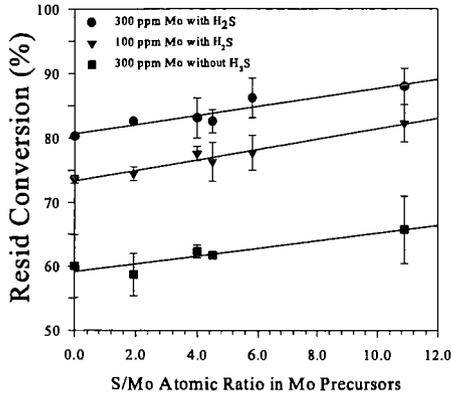


Figure 2. Effect of S/Mo ratio in precursors on resid conversion in the presence/absence of external H₂S.

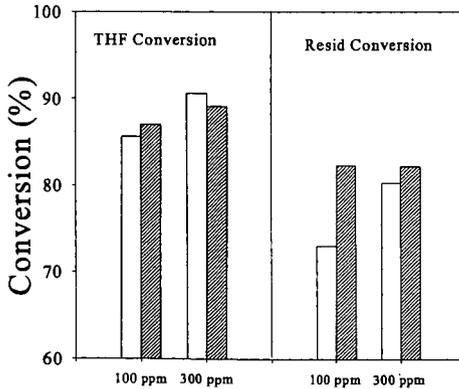


Figure 3. Effect of H₂S/H₂ pretreatment on coal liquefaction with AHM as catalyst precursor. □ --- no pretreatment, ▨ --- H₂S/H₂ pretreatment.