Activities of Molybdenum Based Dispersed Catalyst Precursors

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ABSTRACT

This paper discusses the activation of several Mo-based precursors for coal liquefaction, including various molybdate salts (ammonium, potassium, and nickel), phosphmolybdic acid, and an oil soluble Mo complex (Molyvan L). Except for nickel molybdate which was essentially inactive, the activities of the other precursors towards coal and resid conversions were basically the same. Presulfiding promoted the activity of ammonium molybdate but had almost no effect on the other precursors. The low activity of nickel molybdate is attributed to its stability under liquefaction conditions.

INTRODUCTION

Numerous molybdenum based compounds are readily converted to active dispersed catalysts for coal liquefaction and resid hydroprocessing. These include both inorganic and organic Mo based compounds. The oil soluble Mo precursors are usually dissolved in the reaction system and readily form highly dispersed catalysts. Alternatively, water soluble precursors are impregnated onto the feed coal. During reaction they decompose *in situ* to form an active phases.

Previous liquefaction work in this laboratory has shown that recycled Mo catalyst always gave higher coal and resid conversions than freshly added catalysts. [1] This conclusion was based upon recycled catalyst contained in ashy resid obtained from Wilsonville pilot plant when Wyodak coal was processed with Molyvan L catalyst. The higher activity of recycled Mo catalyst led to the speculation that activation was time dependent and the Mo based catalyst precursors had to experience a few cycles in a continuous process before it could be fully activated. Our recent studies have also indicated that, when sulfur-free ammonium heptamolybdate was used as precursor, complete transformation to active catalyst *in situ* did not occur.[2] However, coals impregnated with thiomolybdates were slightly more active than the oxomolybdates in the absence of added sulfur. We also found that presulfiding oxomolybdate impregnated coal quite significantly increased conversion.

Coal liquefaction using dispersed Mo based bimetallic catalysts has also been widely studied in laboratory-scale batch reactors. The promotional effects of Fe and Ni on Mo catalysts have been reported by a number of researchers using a variety of coals.[3,4,5,6] Synergism was typically explained by the complementary effect of the metals or the formation of a new phase which was responsible for the high activity. However, recent pilot scale test have indicated that introducing Ni and Fe to a molybdenum impregnated coal does not influence conversion.[7]

Although inorganic molybdates have been widely used as catalyst precursors, most of the works has concentrated on ammonium based compounds because of their easy decomposition under liquefaction conditions. The objective of this study is to examine the effectiveness of other non-ammonium based molybdate precursors. Also, since some of these compounds contain more than one type of metal in the molecule, another objective is to examine if there is any advantage to using a compound containing two active metals.

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 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. The following materials were used as received: Molyvan L (8.1% Mo, 6.4% P, R.T. Vanderbilt Co.), ammonium heptamolybdate (AHM, Aldrich,), phosphomolybdic acid (PMA, Aldrich), potassium molybdate (KM, Alfa), nickel molybdate (NiM, Aldrich), and tetrahydrofuran (THF, Aldrich). In all experiments, catalyst loadings were reported as mg Mo per kg dry coal.

Catalyst Pretreatment In some experiments, the catalyst impregnated coal was treated with H_2 containing 8 vol% H_2S prior to reaction. In a typical run, the reactor was loaded with coal slurry and placed horizontally in a furnace after purging with H_2 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 (Techne, 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 H_2 containing 3 vol% H_2S. 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.

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

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

RESULTS AND DISCUSSION

The liquefaction experiments using these catalyst precursors were performed at Mo loadings of 100 ppm and 300 ppm with/without H_2S/H_2 pretreatment. Figure 1 shows that at the Mo loading of 300 ppm without pretreatment, there is essentially no difference toward both coal and resid conversions for Molyvan L, AHM, PMA, and KM. The mean THF coal conversion of these four Mo precursors was 90.1±0.6% and mean resid conversion was 81.1±1.0%. For the Mo catalyst loading of 100 ppm as shown in Figures 2-3, the mean THF and resid conversions were 85.5±0.3% and 74.4±1.2%, respectively. The similar activities of these catalyst precursors, both the oil-soluble organic complex and water-soluble inorganic salts, may imply the formation of a similar active phase under liquefaction conditions. Considering the research work in this laboratory in the past years and those in open literatures, it is suggested that the formation of dispersed molybdenum catalyst is relatively independent of the starting material, as long as they decompose.

When the metal impregnated coal slurry was pretreated with H_2S/H_2, however, the activities of these precursors varied. At Mo loading of 100 ppm with pretreatment, coal conversions with AHM and KM increased slightly while that with PMA decreased. For resid conversion, AHM gave about 9% increase but PMA decreased by 4%, in line with its performance for THF coal conversion. The behavior of PMA in this study is consistent with the observation when this material was presulfided separately and then impregnated on coal.[8] Overall, it appears that pretreatment with H_2S improves the activity of AHM for resid conversion, does not affect the activity of KM, and slightly reduces the activity of PMA for both coal and resid conversions.

The major difference between KM, AHM and PMA is the presence of an ammonium group in AHM. As already noted, the catalyst precursors can not be fully activated *in situ* during a 30 minutes batch liquefaction run. Only a fraction of the precursors are converted to an active phase. Thus, the differences in activities between precursors may not be distinguishable. When these precursors are subjected to pretreatment, AHM is converted to an active phase through loss of the ammonium group. Thus, AHM exhibited higher activity than the other two precursors. Of course, over a longer period of exposure, such as that in a continuous process with catalyst recycle, most of the precursor would have converted to an active phase. As a result, these precursors show similar activities, although their activation kinetics may be different. The pilot plant test results indicated essentially no activity difference between AHM and PMA precursors. [7]

An interesting observation was that NiM improved coal conversion by less than 5% and resid conversion by less than 3% at all conditions tested. The low activity of NiM can be attributed to its stability under liquefaction conditions. TG analysis of NiM showed that this material is very stable in He at temperatures up to 600 °C. In $H_2S/H_2/He$ containing 5 vol% H_2S, there was a 1.5% weight gain at 450 °C indicating insignificant addition of sulfur, which is necessary to create an active catalyst phase. Unlike other Mo-based precursors, NiM is not readily converted to nickel and molybdenum sulfides that are active toward coal liquefaction. Therefore, NiM showed almost no advantage over thermal runs. In contrast, AHM and PMA have both been reported to form active phases [8,9] and showed high activities for both coal and resid conversions.

CONCLUSIONS

The inorganic and organic molybdenum compounds tested in this study showed essentially the same activities towards coal liquefaction and resid conversion. The nature of catalyst precursors is different and their activation mechanism may vary. In batch reactors which are typical of short reaction time, these precursors may exhibit different activities. It is expected, however, that in a continuous process with Mo catalyst recycle, the catalyst activity will be independent on precursor type as long as they decompose under liquefaction conditions. The low activity of nickel molybdate is probably due to its stability under liquefaction conditions.

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Table 1. Properties of Wyodak Coal and Feed Solvent

	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		

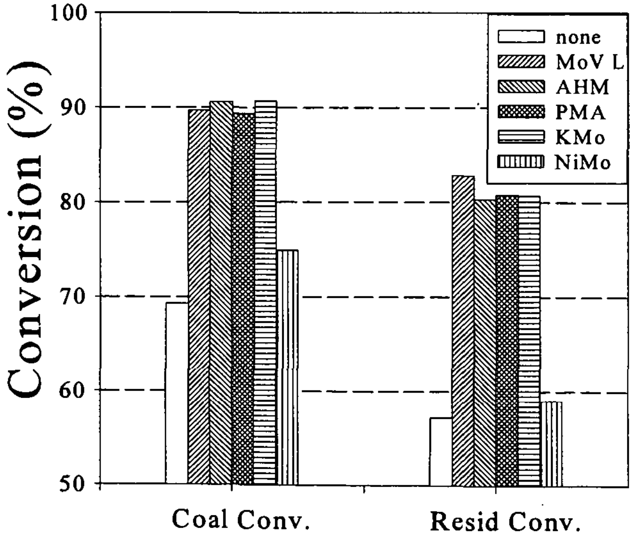

Figure 1 Effect of Various Mo Based Catalyst Precursors on THF Coal and Resid Conversions with Mo Loading of 300 ppm.

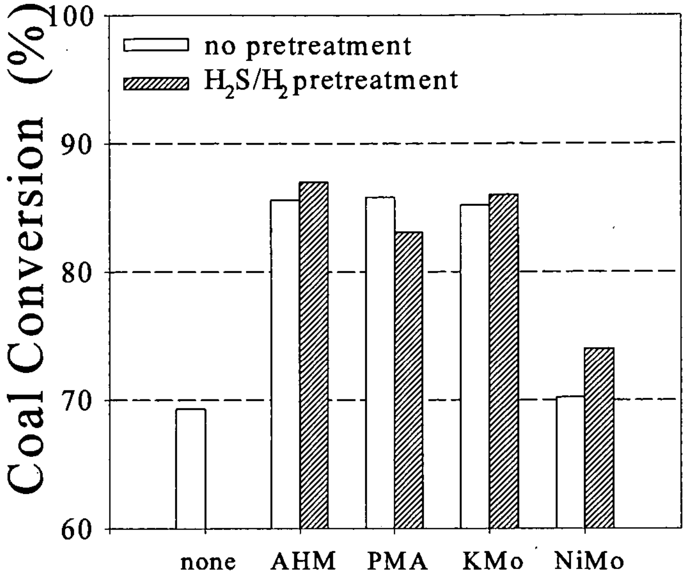

Figure 2 Effect of H_2S/H_2 Pretreatment on THF Coal Conversion with Mo Loading of 100 ppm

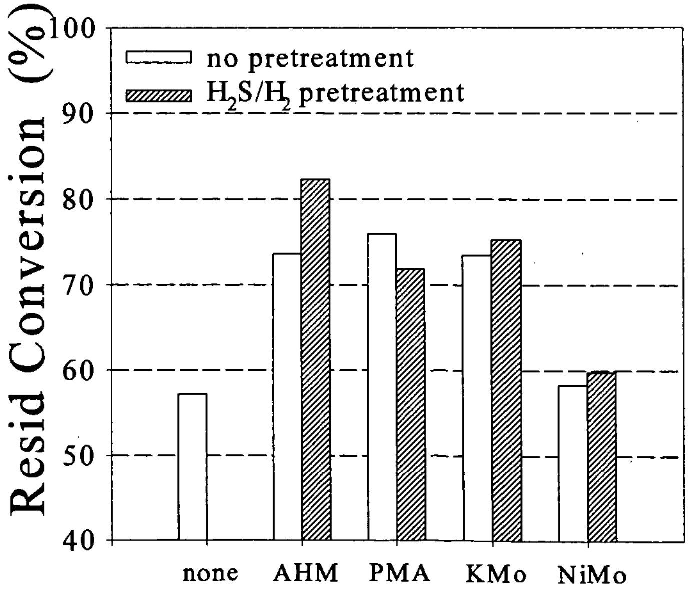

Figure 3 Effect of H_2S/H_2 Pretreatment on Resid Conversion with Mo Loading of 100 ppm