

ASSESSMENT OF BIMETALLIC AND PARTIALLY-SULFIDED PHOSPHOMOLYBDATES FOR LIQUEFACTION OF WYODAK COAL

Belma Demirel, Chad M. Adams and Edwin N. Givens
University of Kentucky Center for Applied Energy Research
2540 Research Park Drive, Lexington, KY 40511-8410

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ABSTRACT

Phosphomolybdic acid (PMA) is an excellent catalyst precursor for direct liquefaction of Wyodak coal when well dispersed within the reaction system by impregnating onto the feed coal. Addition of sulfur during the reaction significantly increased the activity of the catalyst. Several partially sulfided phosphomolybdates were prepared and characterized by a variety of analytical techniques. THF and resid conversions with these partially converted precursors were determined when added as particulate material directly to the reaction mixture and when impregnated onto Wyodak coal. The effectiveness of these partially converted intermediates will be related to their physical characteristics and elemental and structural compositions. Nickel and cobalt bimetallic phosphomolybdates were prepared and impregnated on coal. The effect of the co-metal on the activity for solubilizing coal and conversion of coal-derived resid will be compared with other active Mo precursors.

INTRODUCTION

Development of catalysts is important for more efficient coal liquefaction to produce liquid fuels. Dispersed catalyst is understood as the catalytic material employed as particles dispersed on coal or in the reaction media. It provides intimate contact with the surface of coal particles which influence reactions and break the coal structure to gas and liquid products. Many reports have been published on liquefaction using dispersed catalysts, particularly molybdenum and iron sulfide. Molybdenum is often added to liquefaction processes either as the oxide or thiolate water-soluble salts or as molybdenum naphthanate.¹ The active form of molybdenum is not well-known, although it is considered to be molybdenum disulfide. Our studies indicate that intermediate molybdenum oxysulfides may be the active catalyst.^{2,3} Lopcz et al. reported that the atomic S/Mo ratio was less than two in the active catalysts isolated from processing heavy petroleum fractions with ammonium molybdate and thiomolybdate.⁴

Most active catalysts are insoluble in common solvents and one method of increasing dispersion is to introduce the catalyst as a soluble precursor.⁵⁻⁸ Phosphomolybdic acid (PMA) and most bimetallic phosphomolybdates are soluble in water and provide good dispersion.⁹ When PMA was impregnated onto coal, THF and resid conversions are comparable to those obtained from various molybdenum salts.^{3,10-12}

The addition of a second metal, such as Ni and Co, can increase hydrogenation and hydrodesulfurization activity. Chiantelli et al. used bimetallic complexes to study the promotional effects of Ni and Co for MoS₂.¹³ Garg and Givens reinvestigated the catalytic activity of several impregnated transition metals in coal liquefaction and showed that addition of Ni, Co and Mo salts was effective.² Eccless and de Vaux reported that Ni-Mo or Co-Mo gives a very high yield of light oil fractions.¹⁴

The first objective of this work is to show the performance of sulfided catalysts produced from PMA for coal liquefaction. The second objective is to show the catalytic activities of bimetallic phosphomolybdates for coal liquefaction and to compare them to PMA.

EXPERIMENTAL

Wyodak coal from the Black Thunder Mine in Wright, Wyoming was supplied by Hydrocarbon Technologies, Inc. Proximate and ultimate analysis of the coal are given in Table 1. The recycle solvents were obtained from the Advanced Coal Liquefaction R&D Facilities at Wilsonville, Alabama. Phosphomolybdic acid (PMA) was supplied by Aldrich Chemicals Inc. Co₃(PMo₁₂O₄₀)₂ · xH₂O (CoPM), Ni₃(PMo₁₂O₄₀)₂ · xH₂O (NiPM) and K₃PMo₁₂O₄₀ · xH₂O (KPM) were synthesized in our laboratory.

Sulfidation of PMA was carried out in a 9" x 2" tubular quartz reactor equipped with a furnace, thermocouple and temperature controller. A stream of nitrogen or 8 vol% hydrogen sulfide in hydrogen flowed into the reactor through flowmeters. The exhaust gases from the reactor were passed through a H₂S scrubber filled with NaOH solution and vented to a hood. About one gram of PMA in a porcelain boat was placed into the reactor for sulfidation experiments. After the reactor was purged with nitrogen at ambient temperature to remove air, a stream of 8 vol% H₂S in H₂ was

passed over the sample and the reactor heated to 125, 150, 200, 300 or 450°C. The samples remained at the specified temperature for 4 h at a H₂S-H₂ flow rate of 80 ml/min. In each experiment, a total of 19.2 liters of H₂S-H₂ was passed over the sample. The reactor was subsequently cooled to ambient temperature under nitrogen, and sulfided catalysts (PMA125, PMA150, PMA200, PMA300 and PMA450) were ground to fine powder before use.

Sulfided PMA materials were added to the reaction media in two ways: direct addition of sulfided PMA materials to the reaction mixture and impregnating sulfided PMA materials onto coal. The apparent water solubility of the sulfided PMA materials decreased as the temperature of preparation increased. Coals were prepared by slowly adding in a dropwise manner the water solutions containing the sulfided materials, and any undissolved material, which was normally quite small, was washed onto coal with additional water. Total amount of water used for impregnating the sulfided PMA materials was about 0.5 g per g dry coal. Coals were then dried in a vacuum oven at 96°C and 33 kPa overnight to remove essentially all of the moisture.

The Ni, Co and K salts of PMA were impregnated onto coal from aqueous solutions. The potassium salt was soluble only after adding a few drops of KOH to the water. Coals were impregnated by adding aqueous solutions (0.03 g solution/g dry coal) that contained the appropriate concentration of the individual metal salts to provide a final loading of 300 mg Mo/kg dry coal. During addition, the powdered coal was continually stirred to assure even dispersion. Impregnated coals were used without being dried and contained 11.9 wt% moisture.

Activity tests were carried out in a 50-cc micro autoclave at 440°C and 1350 psig for 30 minutes. The reactor was equipped with a thermocouple, and connected to pressure transducer for monitoring temperature and pressure during the reaction. Experiments were duplicated at least 2 times to confirm the reproducibility. In a typical experiment, 1.75 g of 524°C-distillate (Wilsonville Run 258 period B), 2.8 g of deashed resid (Wilsonville Run 258 period A) and 2.45 g of metals impregnated coal were added to the reactor and pressurized with H₂S/H₂ (3 wt% H₂S in H₂). The reactor was submerged in a fluidized sand bath and agitated continuously at the rate of 400 cycles per minute at the specified temperature. After quenching, solid and liquid products were removed from the reactor using tetrahydrofuran (THF) and the mixture was extracted in a Soxhlet extractor overnight. The THF insoluble fraction was dried in a vacuum oven and weighed. The soluble fraction was distilled under vacuum (modified ASTM D-1160-87) to atmospheric equivalent end point of 524°C to determine the resid and coal conversions.

$$\text{Resid Conv} = \left(1 - \frac{(\text{IOM} + 524^\circ\text{C}^+ \text{Resid (af)})_{\text{Products}}}{(\text{coal (maf)})_{\text{Feed}}} \right) \times 100$$

RESULTS AND DISCUSSION

Molybdenum compounds are widely used in coal liquefaction because of their hydrogenation activity and the ease which they can be dispersed in the reaction system or impregnated onto coal. Sulfur or sulfided catalysts are generally added to the reaction mixture to convert them to the sulfided forms under reaction conditions.¹⁵

PMA was sulfided at elevated temperatures in order to understand the form of the catalyst derived from the precursors.¹⁶ Elemental analysis of presulfided materials are given in Table 2. The activities of these materials were determined by adding these particulate solids to the reaction mixture and by impregnating them from an aqueous solution onto coal. The activity resulting from adding the particulate presulfided materials directly to the reaction mixture was much less than observed by impregnating untreated PMA onto coal (Figure 1). THF conversions decreased as the treatment temperatures increased. They were about 62% for materials treated between 125 and 200°C and decreased to about 57% for materials prepared at 300 and 450°C. The THF conversion for untreated particulate PMA was 80.7%. Resid conversions (maf) for the sulfided materials varied between 43-48% while untreated particulate PMA gave 42.7%.

Good dispersion of the catalyst on the surface of the coal particles improves conversion by increasing the amount of active surface area in the reaction phase. An approach to achieving catalyst dispersion is to employ a solvent for dispersing the catalyst. Unfortunately, liquefaction catalysts such as pyrrhotite, pyrite and molybdenum sulfide are insoluble in all common solvents. Although the soluble precursors may not be catalytically active they transform into active catalysts at elevated temperatures. As an example, the water soluble PMA, which decomposes to intermediate molybdenum oxysulfides at typical liquefaction temperatures, has been used as a precursor to obtain a good dispersion.⁷

Because of the partial solubility of the sulfided PMA materials in water, they were impregnated onto coal from aqueous solutions. The activity of the impregnated coals was higher than observed for the particulate addition of the sulfided materials but not as high as observed for PMA impregnated coal (Figure 2). Both THF and resid conversions were higher for those materials

prepared at the lower temperatures. THF conversion for PMA125 is only slightly less than the PMA impregnated coal, i.e., 89.2 and 92.3%, respectively. Resid conversions varied from 65 to 42% with PMA125 and PMA150 giving essentially the same resid conversion as PMA impregnated coal (64.5%). Higher treatment temperatures resulted in a significant decrease in resid conversions. Although the data indicate that the sulfided materials prepared at lower temperatures are as active as PMA, they do not show any improvement over impregnated untreated PMA.

Activities of metal impregnated coals were compared in Figure 3. Nickel phosphomolybdate (NiPM) and cobalt phosphomolybdate (CoPM) gave almost the same average THF conversions, which was somewhat higher than the average conversion for potassium phosphomolybdate (KPM). The THF conversion for PMA (92.3%) was slightly higher than the Co and Ni salts. The standard deviations for the salts showed significant overlap in the values suggesting no significant difference in these conversions, although the PMA value appears to have statistical significance. The resid conversion of NiPM was higher than the Co and K salts although standard deviations again indicated significant overlap in the values. The NiPM resid conversion is also greater than observed for the PMA impregnated coal (64.5%).

CONCLUSION

Sulfided PMA materials did not show higher catalytic activity than PMA when added directly to the reaction media, and gave lower THF conversion than the non-catalyzed thermal case. The activities of impregnated sulfided PMA materials prepared at 125 and 150°C was comparable to PMA. Conversions decreased for sulfided materials produced at higher temperatures. Apparently, materials prepared at the higher temperatures are not as well dispersed due to their decreasing solubility in water. None of the bimetallic phosphomolybdates (CoPM, NiPM and KPM) improved THF conversion, however resid conversion was higher for NiPM than for the other bimetallic salts or untreated PMA. Resid conversion for CoPM was comparable PMA.

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Table 1. Analysis of Wyodak Black Thunder Coal.

Proximate Analysis	w%	Ultimate Analysis	w%(dry)	Sulfur Analysis	w%
Moisture	8.89	Carbon	70.62	Total	1.94
Ash	5.76	Hydrogen	5.03	Pyritic	0.80
Volatile matter	39.88	Nitrogen	1.13	Sulfate	0.80
Fixed carbon	45.47	Sulfur	0.52	Organic	0.34
		Oxygen (diff)	16.38		
		Ash	6.32		
		Ash, SO ₃ -free	5.47		

Table 2. Elemental analysis of PMA and the sulfided samples.

S/Mo atomic ratio in feed = 12.3

Sulfidation time = 4 h

	Composition, wt%				Formula
	P	Mo	S	O (diff) ^a	P _x Mo ₁₂ S _y O _z
PMA	3.52	49.65	0.00	46.83 ^b	H _{45.6} P _{2.6} Mo ₁₂ O _{65.8} (H ₃ PMo ₁₂ O ₄₀ · 20H ₂ O)
PMA125	4.26	59.50	4.95	31.29	P _{2.7} Mo ₁₂ S _{3.0} O _{37.8}
PMA150	4.57	60.97	5.40	29.06	P _{2.8} Mo ₁₂ S _{3.2} O _{34.3}
PMA200	4.74	65.60	4.79	24.87	P _{2.7} Mo ₁₂ S _{2.6} O _{27.3}
PMA300	5.48	66.49	4.93	23.10	P _{3.1} Mo ₁₂ S _{2.7} O _{25.0}
PMA450	5.31	70.11	20.60	3.98	P _{2.8} Mo ₁₂ S _{10.6} O _{4.1}

a. Difference includes oxygen and hydrogen

b. Includes 3 wt% hydrogen

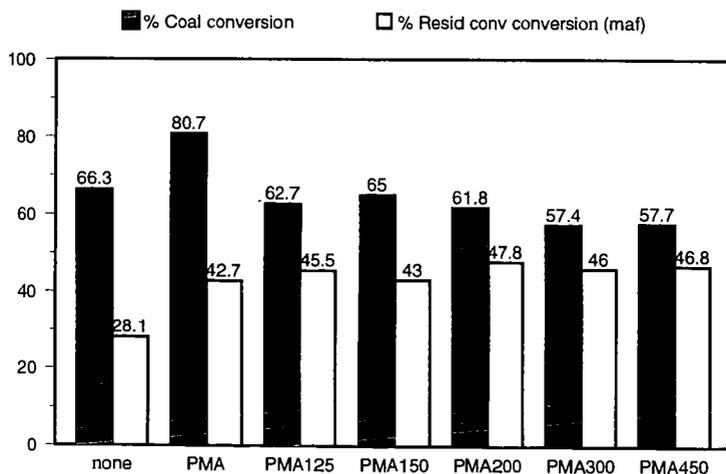


Figure 1. Activity tests from direct addition of PMA and the sulfided PMA materials to reaction mixture.

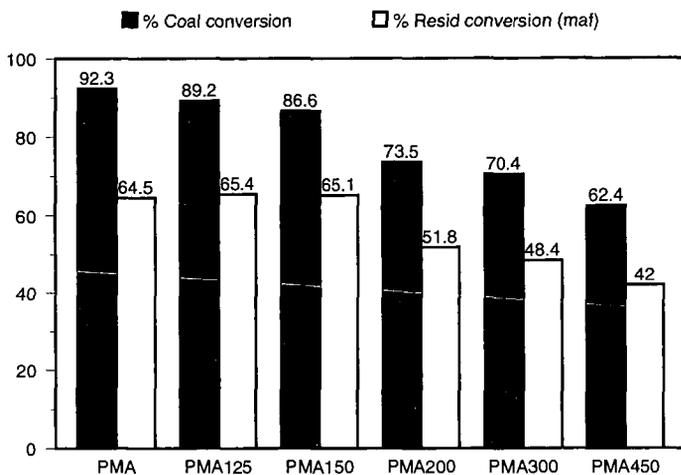


Figure 2. Activities of coal impregnated with PMA and the sulfided PMA materials.

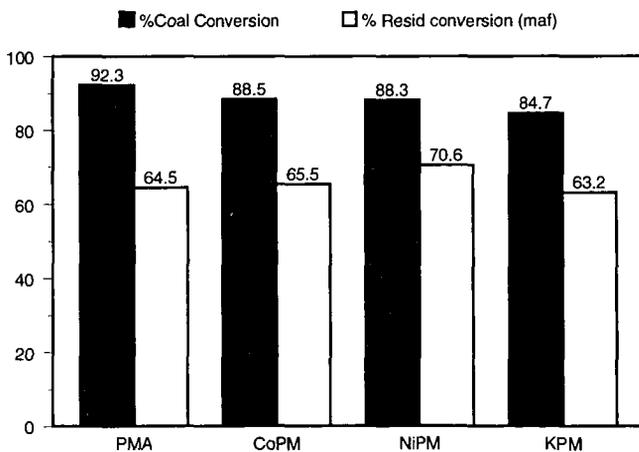


Figure 3. Activities of coal impregnated with PMA, CoPM, NiPM and KPM.