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Transformation of phosphomolybdic acid into an active catalyst with potential application in coal liquefaction

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Abstract

Since phosphomolybdic acid (PMA) is known to be transformed into an active catalyst for liquefying coal and converting the residual product to distillate material, its conversion under conditions similar to those used in liquefaction has been investigated. The form of active catalyst formed from PMA under conditions of liquefaction is unknown. This paper reports the reaction of PMA observed in He, H_2 and H_2S–H_2 at temperatures up to 450°C. PMA is stable in both He and H_2 up to 200°C. However, when H_2S is present, sulfur is incorporated rapidly into the structure. The amount of incorporated sulfur increases both with temperature and exposure to H_2S. At temperatures up to 300°C, the maximum incorporation of sulfur was approximately 5 wt.% to give a material having a S/Mo atomic ratio of 0.27. Exposure to a large excess of H_2S did not further increase incorporation of sulfur. At 450°C, which is the temperature required for liquefaction of coal, approximately 20 wt.% sulfur was incorporated to give a S/Mo atomic ratio of 0.88. In this sample, the remaining oxygen was present as P_2O_3. IR and Raman spectra showed the presence of MoS_2, although insufficient sulfur was present to completely convert Mo to its disulfide. When H_2S is present, even at 125–150°C, the crystalline structure collapses destroying the Keggin structure. The rate of sulfur addition to PMA is much faster for MoO_3, than for MoO_2. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Phospomolybdic acid; Sulfides; Coal liquefaction; Catalyst

1. Introduction

In recent years, extensive data have been obtained which show that molybdenum introduced as a variety of precursors forms a very active catalyst for liquefaction of Wyodak coal. Molybdenum di(2-ethylhexyl)-phosphorodithioate (Molyvan L) was found to be exceptionally active in tests at the Wilsonville Advanced Coal Liquefaction Research Facility in runs 263 [1] and 262 [2]. *N*,*N*-dibutyldithiocarbamate of oxothiomolybdenum (Molyvan A) was as active as Molyvan L in runs made at Exxon [3,4]. We reported recently that THF solubilization and resid conversions for Wyodak coals impregnated with PMA in microautoclave tests was comparable to results with Molyvan L and Molyvan A, which were added as oil-soluble complexes [5]. Subsequently, we found that PMA impregnated Wyodak Coal in continuous runs gave similar quinoline solubilization and resid conversion as Molyvan A at the same processing conditions and Mo catalyst concentrations [6]. The activity of PMA was essentially the same as observed for coal impregnated with ammonium heptamolybdate, another precursor that has been extensively studied.

Although few papers have been published, numerous patents have been issued that claim polyoxomolybdates as sources of dispersed catalysts for coal and

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heavy petroleum conversion. Though most of the reported work relates to conversion of petroleum related heavy hydrocarbons, there are patents that describe the use of PMA in conversion of coal. Gleim and Gatsis, [7] in a very early case, claimed a process incorporating PMA for hydrorefining a petroleum oil at 400°C and 10 MPa. In this case, PMA was added to the reaction mixture as an isoamyl alcohol solution, which presumably forms a colloidal dispersion when the isoamyl alcohol is removed by distillation at 130°C [8]. In the hydroconversion of Wyodak coal, a higher oil yield and lower coke make were reported for PMA relative to molybdenum naphthenate, both of which were claimed to be soluble in the heavy distillate solvent [9]. In another case, addition of phenolic solutions of PMA to coal slurries was reported to give higher liquid yields [10]. Several cases claim preparation of catalyst concentrates by mixing either aqueous or isopropyl alcohol solutions of PMA with oil and heating at 385°C for 30 min in 5% H_2S in H_2 [11–14]. Adding phosphoric acid or hydrogen halides to PMA has been reported to improve catalyst activity [15,16]. Combinations of MoO_3 and PMA have also been reported to give better resid conversion than the individual compounds [17–19].

PMA is a unique form of Mo having the Keggin structure [20]. It has already found extensive use as a catalyst in a number of other processes involving both homogeneous [21] and heterogeneous [22] catalysis. Typically, these reactions are run at lower temperatures than required for liquefaction of coal. Although catalysis at these lower temperatures is attributed to the presence and stability of the Keggin structure, little is known regarding the structural stability of PMA at the higher temperatures necessary for liquefaction, especially in the presence of H_2 and H_2S.

Since higher activity is achieved for all of the Mo precursors including PMA when H_2S is present, whether the ultimate catalyst is the same when using PMA is not known. When using AHM as precursor, Lopez et al. suggested that the active catalyst was an undefined molybdenum oxysulfide [23]. This conclusion was based upon the atomic ratio of sulfur to molybdenum in the active catalysts isolated from processing heavy petroleum fractions with ammonium molybdate and thiomolybdate precursors, which was less than two. Surprisingly, they found that several less active catalysts isolated from processing petroleum fractions had S/Mo ratios greater than two suggesting that MoS_2 had a lower activity than the active catalyst.

Because of the unique thermal stability of PMA, it is not obvious that the form of the active catalysts from this family of compounds will be the same as obtained from oxo or thiomolybdates. Likewise, it is not known whether sulfur may incorporate into these structures giving thio analogs of the polyoxomolybdates that may be active for catalyzing direct liquefaction. For these reasons, we have investigated the thermal properties of PMA and its reaction in the presence of H_2S–H_2 mixtures. The objective was to understand the form of the catalyst derived from the precursor and improve its activity through altering the reaction conditions or pretreating the precursor.

2. Experimental

Phosphomolybdic acid ($H_3PMo_{12}O_{40}\cdot 20H_2O$) was supplied by Aldrich Chemical Company. Gases were supplied by Air Products and Chemicals.

Sulfidation experiments were conducted in a $9'' \times 2''$ tubular quartz reactor into which was placed a porcelain boat containing from 1–10 g of PMA. In experiments with one gram PMA, only a thin layer coated the bottom of the porcelain boat. The reactor was placed into a tubular furnace equipped with a thermocouple and temperature controller and a stream of N_2 passed over the sample. After the reactor was purged with nitrogen at ambient temperature to remove air, a stream of 8 vol% H_2S in H_2 was passed over the sample and the reactor heated to the desired temperature. The H_2S–H_2 mixture was passed over the samples for 1–10 h at 40–320 cc/min. Following the treatment the reactor was cooled to ambient temperature under flowing N_2 and the products removed. In the experiments the original yellow color changed quickly to green, which lasted for only a short period. All of the samples formed crusty layers that were either dark grey or black in color. The final materials were ground before analyzing.

Elemental analyses were performed either by the University of Kentucky Center for Applied Energy Research or by Galbraith Laboratories. At both laboratories sulfur was determined by combustion in air and molybdenum and phosphorus by inductively coupled plasma emission spectroscopy. Samples analyzed by

Galbraith Laboratories had confidence intervals of 5.3%, 0.4% and 0.3% for molybdenum, sulfur and phosphorus, respectively.

Raman scattering measurements were carried out by excitation with an Ar laser (514.5 nm). Scattered light was analyzed at a low laser flux (30 mW/mm^2) in a Jobin Yvon HR460 single grating spectrometer equipped with a charge-coupled array detector and a holographic notch filter (Kaiser Optical). The spectral slit width of the system is about 2 cm^{-1}.

FT-IR spectra were obtained with a Bomem DA3+ Fourier transform interferometric spectrometer. For mid-IR measurements, the samples were mixed with 99 wt.% of KBr and pressed into pellets. For far-IR measurements, the samples were mixed with 99 wt.% of CsI. A MCT detector and a bolometer were used for mid-IR and far-IR data acquisition, respectively. All spectra were taken at room temperature with an instrument resolution of 4.0 cm^{-1}.

X-ray diffraction data were obtained with a Philips XRG 3100 diffractometer in the range of 10–80° (0.02°/step and 2 s/step). The JSPDS-ICDD Powder Diffraction-2 Database was used for identification of the samples.

A Seiko TG/DTA 320 thermogravimetric analyzer (TGA) was coupled to a VG Micromass PC quadrupole mass spectrometer. The thermal analyzer was operated at a gas flow rate of 200 cc/min at a heating rate of 20°C/min up to 650°C. The gas sample was transferred from the thermogravimetric analyzer to an inert Metrasil molecular leak that interfaced the capillary with the enclosed ion source of the mass spectrometer. The mass spectrometer had a Nier-type enclosed ion source, a triple mass filter and two detectors (a Faraday cup and a secondary emission multiplier). Both instruments were controlled by computers that also provided programmable control of the furnace, continuous weight measurements, sweep gas valve switching, data acquisition and analysis, review of mass spectrometer scans and export data to other computers.

3. Results

3.1. Thermogravimetric analysis

PMA is thermally stable up to a rather high temperature. When heated in a TGA in He, an initial decrease in weight at temperatures up to 150°C corresponds to the loss of crystalline water, or water of hydration, via an endothermic process. This is confirmed by the appearance of an $m/e = 18$ ion in the mass spectrum of the effluent gas (Fig. 1). Between 150°C and 350°C, only a slight additional loss in weight occurs. However, continued heating up to 450°C results in further loss in weight and appearance of water in the effluent gas stream. The latter decrease in weight corresponds to a loss of 1.5 molecules of water, commonly referred to as constitutional water, for each molecule of dehydrated PMA. Ultimately P_2O_5 and MoO_3 are reportedly formed via the reaction in Eq. (1)[24].

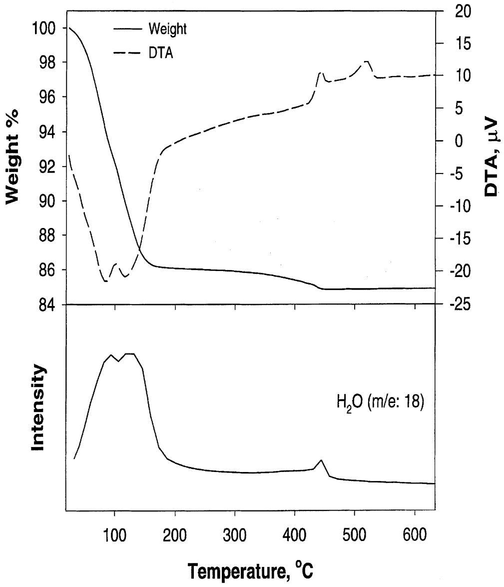

Fig. 1. TG/MS spectra of PMA in He.

$$3H_3PMo_{12}O_{40} \rightarrow 3H_2O + P_2O_5 + 25MoO_3 \tag{1}$$

When the TGA is run in the presence of H_2, dehydration is essentially the same as in He. The subsequent loss of 'constitutional' water begins at a lower temperature (~350°C) than observed in He (~425°C) and proceeds over a longer period (compare Figs. 1 and 2). In H_2, the weight loss upon heating to 470°C is consistent with the formation of MoO_3. Continued heating to 530°C leads to further loss in weight and formation of water. The decrease in weight is consistent with formation of MoO_2. This contrasts with the results of Yong et al. [25] who observed

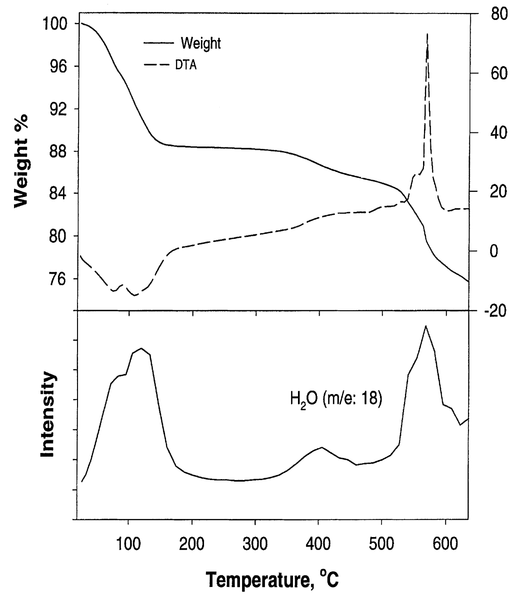

Fig. 2. TG/MS spectra of PMA in H_2.

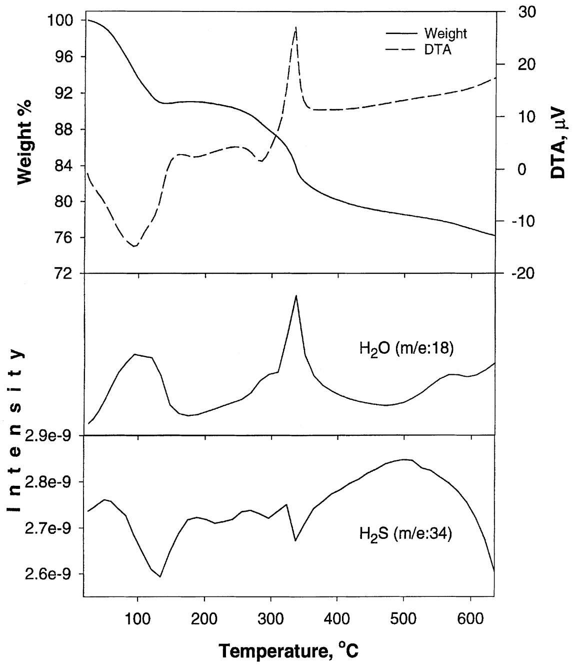

Fig. 3. TG/MS spectra of PMA in H_2S/H_2.

complete reduction to fine Mo powders upon extended heating at temperatures up to 640°C.

H_2S, which is essential for developing active catalyst from PMA for liquefaction of coal, affects the behavior of PMA. When H_2S is present in the H_2 carrier gas, the initial decrease in weight and formation of water at temperatures up to 150°C are similar to the TGA scans made in both He and H_2 (Fig. 3). Simultaneously, the H_2S concentration in the effluent gas was observed to decrease by approximately 5%. The H_2S removed from the gas stream was at least 3 times the initial weight of the TGA sample. Since the decrease in weight of the sample in the presence of H_2S is the same as observed in He and H_2, an increase in the concentration of sulfur in the sample could not account for H_2S lost from the gas stream.

Upon continued heating to about 250°C in the presence of H_2S, the sample weight remains relatively constant and the concentration of H_2S in the effluent stream returns to its original baseline concentration. Further heating to 350°C resulted in an additional loss in weight accompanied by the appearance of water and a simultaneous decrease in H_2S concentration in the effluent gas. The weight loss was less than observed at the lower temperature. During these periods when H_2S disappeared from the gas stream, it must have been converted and the products swept out of the system in the flowing gas. SO_2 was not observed in the effluent gas stream over the entire temperature range indicating that H_2S was not converted to sulfur oxides in a quantity that could be detected. The presence of a sulfur deposit found in the exit line from the TGA suggests that H_2S is being converted to free sulfur.

3.2. *Treatment of PMA with H_2S*

Since TGA scans of PMA in H_2–H_2S suggest that sulfur was not being incorporated into the structure, larger quantities of material were prepared to quantify the amount of incorporated sulfur and the properties of these materials. PMA was treated in a tubular reactor in flowing H_2S–H_2 at atmospheric pressure and at 125–450°C for 1–10 h. These treatments were performed over a range of different gas flow rates that exposed the samples to quantities of sulfur that ranged from 0.3 to 123 moles H_2S/g atom Mo. After cooling, the dark colored materials were removed from the reactor, ground and stored in sealed containers to limit exposure to air. The solubility of the sulfided materials in water at a concentration of 0.2 wt.% decreased with

Table 1
Sulfur concentration in sulfided PMA materials

H_2S/Mo ratio in treatment gas (moles/g atoms)	Temperature (°C)	Treatment period (h)				
		1	4	6	8	10
0.3[a]	125	1.48 (0.07)	–	–	–	–
0.3[a]	150	2.13 (0.10)	–	–	–	–
0.3[a]	200	1.21 (0.06)	–	–	–	–
0.3[a]	300	2.21	–	–	–	–
0.3[a]	450	4.20 (0.18)	–	–	–	–
12.3	125	3.78 (0.19)	4.95 (0.25)	–	–	–
12.3	150	4.27 (0.21)	5.4 (0.27)	–	–	–
12.3	200	4.46 (0.22)	4.79 (0.22)	3.2 (0.16)	–	–
12.3	300	4.16 (0.20)	4.93 (0.22)	4.35 (0.22)	4.0 (0.21)	–
12.3	450	10.9 (0.47)	20.6 (0.88)	17.25 (0.74)	16.0 (0.67)	–
123	125	–	4.37 (0.22)	–	–	–
123	150	–	3.9 (0.19)	–	–	–
123	200	–	3.77 (0.18)	–	–	–
123	300	–	3.69 (0.18)	–	4.0 (0.20)	–
123	450	–	15.0 (0.64)	17.1 (0.73)	17.7 (0.76)	18.1 (0.78)

[a]Treated 10 g sample.
S in wt.% and S/Mo atomic ratio.

increasing treatment temperatures with none of them being completely soluble. BET surface areas of the materials were typically less than 1 m^2/g. They were characterized by IR, FT-IR, far-IR, XRD, Raman, and elemental analysis.

Sulfur incorporated into the samples was affected both by the relative amount of H_2S passed over the samples and the temperature of treatment (Table 1). At all temperatures, sulfur incorporated into the samples increased as exposure to H_2S increased. Up to 300°C, exposures longer than one hour to H_2S equivalent to a H_2S/Mo molar ratio of 12.3 did not significantly change the sulfur concentration. Differences in concentrations shown in Table 1 may be a result of the analysis having been performed by two different organizations. At higher H_2S exposures, i.e., at a H_2S/Mo molar ratio of 123, sulfur incorporated into the samples was essentially unchanged compared with samples exposed at a 12.3 H_2S/Mo molar ratio. Increasing the exposure time up to 8 h did not greatly affect the sulfur incorporated into the samples.

At 450°C, the sulfur incorporated into the samples increased sharply. When the samples were treated with an excess of H_2S at H_2S/Mo molar treatment ratios of 12.3 and 123 for 1–10 h, the sulfur incorporated into the samples increased significantly. When treating at a H_2S/Mo molar treatment ratio of 12.3, sulfur concentrations nearly doubled from 10.9 wt.% after 1 h to 20.6 wt.% after 4 h. Sulfur concentrations did not change much after treating for 4 h for samples treated at the higher H_2S/Mo molar ratio of 123. Based upon Mo present in the samples the S/Mo atomic ratio never exceeded 0.90 in any of the samples.

For samples exposed to a limited amount of H_2S, a very high percentage of sulfur was scavenged from the gas stream. For samples exposed to H_2S at H_2S/Mo molar ratios of 0.3, the sulfur concentrations in these samples that accumulated over the 1 h treatment period ranged from 1.2–4.2 wt.%. At temperatures up to 200°C, 20–30% of the sulfur present in the gas stream was incorporated into the samples, while at 450°C, 60% was scavenged. Since the sulfur incorporated at temperatures up to 200°C was about half the amount incorporated when treated with a large excess of H_2S, the initial inclusion of sulfur occurs very rapidly. Ultimately a concentration is reached beyond which further exposure to H_2S will not increase the sulfur concentration.

The phosphorus concentrations in samples prepared at a H_2S/Mo molar treatment ratio of 12.3 suggest an excess of phosphorus in the starting material compared with the theoretical Keggin ion formula, i.e., $H_3Mo_{12}O_{40}{\cdot}xH_2O$. The P/Mo atomic ratio remained approximately the same in the sulfided products (see

Table 2
Elemental analysis of PMA and the sulfided samples

Treatment Temperature (°C)	Composition (wt.%)				Formula
	P	Mo	S	O (diff)[a]	(normalized on $Mo_{12.0}$)
Starting PMA[b]	3.5	49.7	0.0	46.8[c]	$H_{45.6}P_{2.6}Mo_{12}O_{65.8}$
125	4.3	59.5	5.0	31.3	$P_{2.7}Mo_{12}S_{3.0}O_{37.8}$
150	4.6	61.0	5.4	29.1	$P_{2.8}Mo_{12}S_{3.2}O_{34.3}$
200	4.7	65.6	4.8	24.9	$P_{2.7}Mo_{12}S_{2.6}O_{27.3}$
300	5.5	66.5	4.9	23.1	$P_{3.1}Mo_{12}S_{2.7}O_{25.0}$
450	5.3	70.1	20.6	4.0	$P_{2.8}Mo_{12}S_{10.6}O_{4.1}$

12.3 moles H_2S/gram atoms Mo in treatment gas. Treatment period 4 h.
[a] Difference includes oxygen and hydrogen.
[b] Theoretical formula: $H_3PMo_{12}O_{40}\cdot xH_2O$.
[c] Includes 3.0 wt.% hydrogen.

Table 2). The apparent excess of phosphorus found in these samples compared with theoretical was presumably a result of an excess of phosphoric acid being occluded in the starting material. Because the hydrogen concentrations in the treated samples are small and since the water of hydration has been removed, the oxygen concentration can be approximated by the unaccounted mass in the elemental composition. This estimate suggests that oxygen decreased as treatment temperature increased with an especially large decrease occurring between 300°C and 450°C.

IR spectra were obtained on the starting PMA and those samples treated with H_2S. The major absorptions for PMA are observed at 1065, 965, 865, 785 and 255 cm^{-1}. For samples treated with H_2S at a H_2S/Mo molar ratio of 0.3 up to 200°C, the spectra change very little (Fig. 4). Intensities of the P–O stretching frequency at 1065 cm^{-1} and a Mo–O stretching frequency at 865 cm^{-1} diminish slightly as temperature increases. Fine structure completely disappeared in the sample treated at 450°C. XRD scans shown in Fig. 5 show all of the samples have remaining crystallinity that differs from the originally hydrated PMA structure. The XRD of the sample treated at 450°C shows the presence of MoO_2, whose oxygen concentration is consistent with reduction of MoO_3 to a lower oxidation state. The absence of any bands in the 600–1000 cm^{-1} region is consistent with the spectrum observed for MoO_2 [26,27].

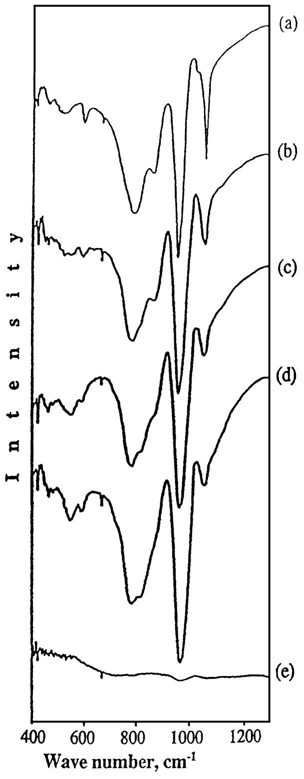

Fig. 4. Infrared spectra of PMA (a) and PMA sulfided at 125°C (b), 150°C (c), 200°C (d), and 450°C (e). H_2S/Mo molar treatment ratio is 0.3.

For samples treated with an excess of H_2S at a H_2S/Mo molar treatment ratio of 12.3, absorptions at 1065 and 255 cm^{-1} largely disappear upon very mild treatment at 125–150°C (see Fig. 6). These bands have been assigned to the stretching vibrations of the P–O and Mo–O bonds of the P–O–Mo group, respectively,

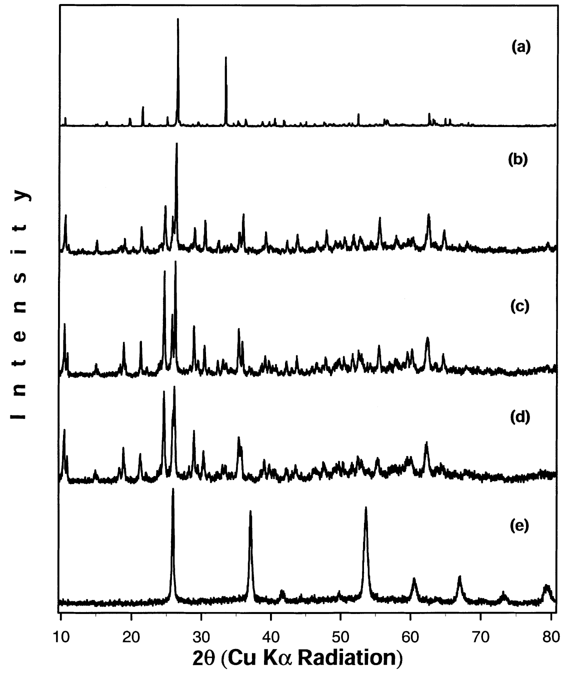

Fig. 5. XRD spectra of PMA (a) and PMA sulfided at 125°C (b), 150°C (c), 200°C (d), and 450°C (e).

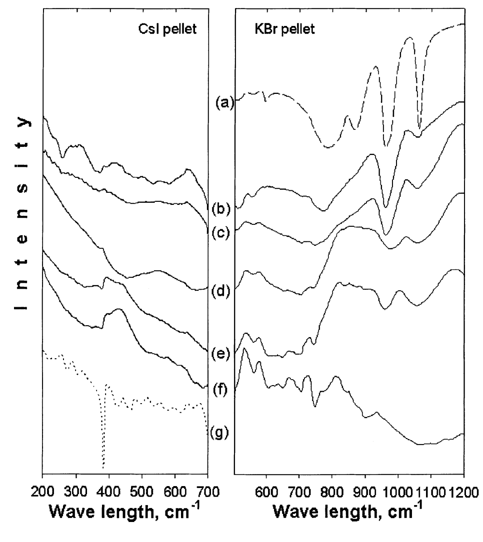

Fig. 6. FT-IR spectra of PMA (a), PMA sulfided at 125°C (b), 150°C (c), 200°C (d), 300°C (e), and 450°C (f), and MoS_2 (g). H_2S/Mo molar treatment ratio is 12.3.

in the Keggin anion [28]. The absorption at 965 cm^{-1}, which has been assigned to the Mo–O asymmetric stretching vibration of the terminal oxygen in the Keggin anion, diminishes slightly but remains strong. The Raman spectra of these mildly treated samples show that the Mo–O stretching vibrations at 975 and 995 cm^{-1} have markedly decreased. The band observed at 255 cm^{-1} assigned to the Mo–O bond of the P–O–Mo group remains strong. A weak shoulder at 225 cm^{-1} increased in intensity in both the 125°C and 150°C treated materials. Elemental analysis of these samples shows that the compositions have changed through loss of water and addition of 5.0 wt.% sulfur. The empirical formula based on the elemental analysis suggests the Mo remains as Mo^{6+}.

IR spectra for samples treated at 200 and 300°C with H_2S at a 12.3 H_2S/Mo molar ratio are similar to each other but quite different from the lower-temperature treated materials. The absorption at 865 cm^{-1} has largely disappeared and the absorption at 785 cm^{-1} has broadened and shifted down field. The intensity of the absorption at 965 cm^{-1} has diminished and broadened indicating continued evidence of Mo bonding with a terminal oxygen atom. For the 300°C treated sample, the absorptions in the Raman spectrum in the 900–1000 cm^{-1} region have largely disappeared. The

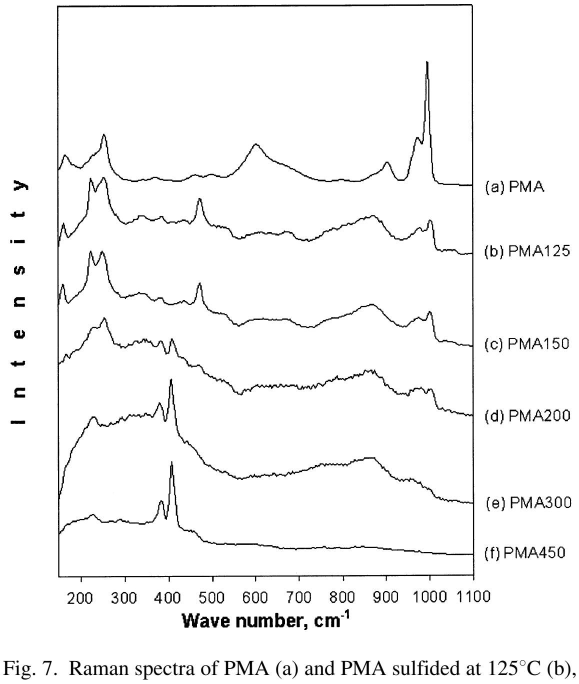

Fig. 7. Raman spectra of PMA (a) and PMA sulfided at 125°C (b), 150°C (c), 200°C (d), 300°C (e), and 450°C (f).

doublet at 225 and 255 cm^{-1} has also disappeared. Elemental analysis shows that the oxygen concentration decreased relative to the amount in the 125–150°C treated samples and the average oxidation state of Mo is less than 4+. The XRD spectra shows that these samples are amorphous.

The IR spectra of the sample treated at 450°C with an excess of H_2S at a H_2S/Mo molar ratio of 12.3 shows a weak absorption at 750 cm^{-1}, which suggests remaining Mo–O bonded structures. A weak absorption at 375 cm^{-1}, also observed in the sample treated at 300°C, is consistent with a Mo–S stretching frequency for MoS_2 [29]. The presence of MoS_2 is further confirmed by the appearance of a doublet at 380 and 405 cm^{-1} in the Raman spectra (see Fig. 7) [30]. XRD shows the material produced at 450°C is amorphous.

4. Discussion

In H_2 at 300°C, the PMA structure is stable. However, at temperatures required for liquefaction, i.e., 420–450 C, the Keggin ion is no longer stable. It decomposes forming MoO_3. In the TGA further decomposition occurs at approximately 530°C through formation of water leading to MoO_2. In liquefaction, transformation into an active catalyst requires the presence of H_2S. Reaction of PMA is dependent on temperature and the H_2S to which it is exposed. When sufficient H_2S is present, regardless of temperature, the structure collapses, although in the presence of a limited amount of H_2S, the structure is stable to at least 200°C.

The initial reaction with H_2S occurs as water of hydration is being lost and is complete at 200°C. When exposed to a limited amount of H_2S PMA scavenges 20–30% of the sulfur from the gas stream forming a solid containing 1–2 wt.% sulfur. Mo remains in a 6+ oxidation state and bands representative of the Keggin anion are observed in the IR and Raman spectra. Continued exposure to H_2S, however, results in further addition of sulfur and an apparent collapse of the structure although only about 4 wt.% sulfur is incorporated. With continued exposure to additional H_2S, the sulfur concentration changes very little. The strongest indication for collapse of the structure is the disappearance of various bands associated with the P–O and Mo–O bonds and the complete absence of any crystallinity, since XRD shows the samples are amorphous.

Since MoO_3 may be an initial decomposition product during liquefaction, it may account for the high degree of sulfidation that occurs in these samples. Arnoldy et al. showed that MoO_3 is sulfided at lower temperatures than MoO_2 in the presence of a H_2S–H_2 stream [31]. Our experiments showed that sulfidation of MoO_3 at 450°C for 4 h incorporates 3.9 wt.% sulfur, which corresponds to $MoS_{0.2}O_{0.9}$. In the samples treated at 450°C, Mo is not completely converted into the disulfide although the IR and Raman spectra indicate its presence. Based upon the elemental concentrations of phosphorus and oxygen and the relative free energies of formation of Mo and phosphorus oxides and sulfides, the phosphorus is probably present as P_2O_3. At the liquefaction reaction temperature in H_2S–H_2, conversion of Mo oxides to the disulfide and P_2O_5 to P_2O_3 is thermodynamically favored. The concentrations of phosphorus and oxygen in the sample are consistent with the presence of P_2O_3 and the resulting S/Mo atomic ratio is approximately one.

These bulk conversions that occur in a bed of crystalline solid may not be entirely indicative of the transformations that occur to Mo compounds molecularly dispersed over the surface of the reactive coal. Other reactants are present which can interact with the PMA and its primary decomposition products, which may alter the ultimate form of the converted precursor. The form of the resulting catalyst may be quite different from the material isolated in these H_2S–H_2 treatment experiments. The experiments show that PMA is more reactive toward H_2S–H_2 than Mo oxides incorporating more than four times as much sulfur at 450°C than MoO_3. It is conceivable that the enhanced reactivity is associated with the unique porosity of the material that develops as dehydration progresses allowing better contact between the Mo structure and the sulfiding agent.

5. Conclusions

The effect of a sulfiding agent on the reaction of PMA in the presence of H_2 has been studied. Lacking

H_2S, but in the presence of H_2, PMA is stable to temperatures of approximately 350°C losing only its crystalline water at temperatures below 150°C. Above 350°C, additional water is lost resulting in collapse of the Keggin structure with formation of MoO_3 and presumably P_2O_5. When H_2S is present, decomposition is observed at much lower temperatures. Collapse of the structure will accompany addition of as little as 3 wt.% sulfur at temperatures as low as 125–150°C. Although sulfur incorporation will increase only slightly at temperatures up to 300°C, a considerable amount of oxygen remains in the treated material. Initially the sulfur adds with Mo remaining in a 6+ state. However, as temperature increases the oxidation state decreases to less than 4+ at 300°C and even lower for samples treated at 450°C. PMA is more reactive toward H_2S–H_2 than Mo oxides incorporating more than four times as much sulfur at 450°C than MoO_3. The oxygen in the latter sample, if it is entirely associated with the phosphorus, suggests an empirical formula for the phosphorus oxide of P_2O_3. The results strongly suggest that the active catalyst in coal liquefaction would not resemble the Keggin structure and questions whether it differs from other precursors that lead to effective catalysts.

Acknowledgements

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References

[1] Southern Electric International, Inc., Run 263 with Black Thunder Mine sub-bituminous coal and dispersed molybdenum catalyst. U.S. Department of Energy Report DOE/PC/90033-23, Wilsonville, AL, 1992.

[2] Southern Electric International, Inc., Run 262 with Black Thunder sub-bituminous coal. U.S. Department of Energy Report DOE/PC/90033-22, Wilsonville, AL, 1992.

[3] L.A. Bauman, L.A. Coless, S.M. Davis, M.C. Poole, M.Y. Wen, Preprints-Div. Fuel Chem. Am. Chem. Soc. 40(3) (1995) 525.

[4] L.A. Coless, M.C. Poole, M.Y., Wen, Continuous Bench-Scale Slurry Catalyst Testing: Direct Coal Liquefaction of Black Thunder Coal. DOE Contract No. DE-AC22-94PC94051. Topical Report (Draft) No. ERLA.2KW.96(2522), Baton Rouge, LA, July–August 1995.

[5] B. Demirel, E.N. Givens, Liquefaction of Wyodak coal with phosphomolybdic acid, Energy and Fuels, in press.

[6] E.N. Givens, et al., Bench-scale testing of advanced concepts for direct coal liquefaction: evaluation of dispersed Mocatalysts, in: Proc. 1997 Coal Liquefaction and Solid Fuels Contractors Review Conf., 3–4 September 1997, Pittsburgh, PA.

[7] W.K.T. Gleim, J.G. Gatsis, Hydrorefining crude oils with colloidally dispersed catalysts, US Patent 3161585, 15 December 1964.

[8] J.G. Gatsis, Hydrorefining of petroleum crude oil, US Patent 3249530, 3 May 1966.

[9] C.L. Aldridge, R. Bearden, Hydroconversion of coal in a hydrogen donor solvent with an oil-soluble catalyst, US Patent, 7 March 1978.

[10] C.L. Aldridge, R. Bearden, Coal liquefaction process, US Patent 4369106, 18 January 1983.

[11] R. Bearden, C.L. Aldridge, F.X. Mayer, J.H. Taylor, W.E. Lewis. Method of preparing a hydroconversion sulfided molybdenum catalyst concentrate, US Patent 4740489, 26 April 1988.

[12] R. Bearden, C.L. Aldridge, F.X. Mayer, J.H. Taylor, W.E. Lewis, Hydroconversion process using a sulfided molybdenum catalyst concentrate, US Patent 4740295, 26 April 1988.

[13] R. Bearden, C.L. Aldridge, Hydrocracking with aqueous phosphomolybdic acid, US Patent 4637871, 20 January 1987.

[14] R. Barden, C.L. Aldridge, Hydrocracking with phosphomolybdic acid and phosphoric acid, US Patent 4637870, 20 January 1987.

[15] C.L. Aldridge, R. Bearden, Hydroconversion process, US Patent 4196072, 1 April 1980.

[16] R. Bearden, W.C. Baird, C.L. Aldridge, Hydroconversion process, US Patent 4424110, 3 January 1984.

[17] J.G. Gatsis, Catalyst for the hydroconversion of asphaltene-containing hydrocarbonaceous charge stocks, US Patent 5288681, 22 Februry 1994.

[18] J.G. Gatsis, Catalyst for the hydroconversion of asphaltene-containing hydrocarbonaceous charge stocks, US Patent 5474977, 12 December 1995.

[19] J.G. Gatsis, Method of preparing a catalyst for hydroconversion of asphaltene-containing hydrocarbonaceous charge stocks, US Patent 5171727, 15 December 1992.

[20] M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer, New York, NY, 1983, pp. 18–30.

[21] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171–198.

[22] N. Mizuno, M. Misono, Chem. Rev. 98 (1998) 199–217.

[23] J. Lopez, J.D. McKinney, E.A. Pasek, Heavy oil processing, US Patent 4 557 821, 10 December 1985.

[24] G.A. Tsigdinos, Ind. Eng. Chem., Prod. Res. Develop. 13(4) (1974) 267.

[25] W.J. Yong, X.X. Quan, J.T. Zheng, Thermochim. Acta 111 (1987) 325.

[26] R.A. Nyquist, R.O. Kagel, Infrared Spectra of Inorganic Compounds, Academic Press, New York, NY, 1997, vol. 4, Spectrum No. 351.
[27] L.M. Gratton, S. Paglia, F. Scattaglia, M. Cavallini, Appl. Spectrosc. 32 (1978) 310.
[28] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, Inorg. Chem. 22 (1983) 207.
[29] C.H. Chang, S.S. Chan, J. Catal. 72 (1981) 139.
[30] E. Payen, S. Kasztelan, S. Houssenbay, R. Szymanski, J. Grimblot, J. Phys. Chem. 93 (1989) 6501.
[31] P. Arnoldy, J.A.M. van den Heukant, G.D. de Bok, J.A. Moulijn, J. Catal. 92 (1985) 35.