Fiber Optical Micro-detectors for Oxygen Sensing in Power Plants

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ABSTRACT

More $\text{Mo}_6\text{Cl}_{12}$ has been synthesized. We have found that previous ambiguous x-ray powder diffraction results are due to disruption of long-range order in the crystals during the heating stage of the synthesis. The quartz cell heaters have been redesigned and are able to heat the substrate. Initial films have been fabricated and are currently under investigation to determine optimal deposition conditions.

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INTRODUCTION

Maximizing the efficiency of the combustion process requires real-time control of the correct fuel/oxygen ratio. This requires the ability to sense oxygen levels over a broad range of concentrations with fast response times.

Mussell, Newsham, and Ruud previously reported preliminary studies of the synthesis and optical properties of $\text{Mo}_6\text{Cl}_{12}$ -based clusters relevant to this project. [1,2,3] Mussell described the synthesis of the molybdenum clusters, and Newsham gives a good account of the properties of neutral $\text{Mo}_6\text{Cl}_{12}$ clusters and their salts, in both solution and a sol gel matrix. Newsham's data indicate that the photophysical properties of the clusters are maintained in sol gel matrices. To prepare a fiber optic sensor based on $\text{Mo}_6\text{Cl}_{12}$, Ruud dispersed $\text{Mo}_6\text{Cl}_{12}$ in poly[1-trimethylsilyl-1-propyne] (PTMSP), and used a dipping technique to immobilize the composite at the cleaved end of a silica optical fiber. Ghosh and co-workers [4] demonstrated a fast room temperature fiber optic sensor based on oxygen quenching of the luminescence from the PTMSP/ $\text{Mo}_6\text{Cl}_{12}$ composites. While the PTMSP support is adequate for room temperature applications, is unable to withstand the high temperatures associated with combustion in a power plant. To improve the sensor's high temperature performance, we are replacing PTMSP with a thermally stable sol gel matrix that should be able to withstand the higher temperature requirements of the power plant combustion process. The idea of using a sol gel as the support matrix for high temperature oxygen sensor application is not new. Remillard and coworkers have shown that a sol gel supported copper based oxygen sensor can be used in a combustion process [5]. With these facts in hand, we anticipate promising results from our design.

EXECUTIVE SUMMARY

We previously synthesized quantities of $\text{Mo}_6\text{Cl}_{12}$ needed for this project. While uv/vis and emission results indicated that the correct material was prepared, the x-ray powder diffraction results were consistent with the formation of $\text{Mo}_6\text{Cl}_{12}$ with more limited crystallinity than had been described in the literature. Further investigation showed that the difference is related to a post-synthesis processing step used to convert the initially formed $\text{Mo}_6\text{Cl}_{12}$ hydrochloride salt to the neutral $\text{Mo}_6\text{Cl}_{12}$ clusters. Recent x-ray powder diffraction data confirm that the $\text{Mo}_6\text{Cl}_{12}$ hydrochloride salt is highly crystalline. As the salt is heated to drive off the HCl, the long-range order of the clusters is disturbed leading to what appears by x-ray powder diffraction to be amorphous material. Since the basic structure of the clusters, the source of the photophysics relevant to this project, is unchanged by the loss of HCl, we now are cautiously optimistic that we have the material necessary for the remainder of the project. In progress are a detailed series of spectroscopic measurements of the line-shape and degree of oxygen quenching of the newly synthesized $\text{Mo}_6\text{Cl}_{12}$ clusters.

The high temperature photophysical properties of the molybdenum cluster in the form of thin films will be measured in a quartz cell with provisions for heating (up to at least 200 °C) in a controlled gas atmosphere. A platinum heater structure has been developed to enable heating of the thin films, and the electrical contact problems reported previously were solved by using a microwelder. In addition the x-y-z-theta stage for holding the quartz cell has been redesigned to improve the positioning accuracy of the incident pump beam, which will allow us to make repeated measurements of the same area of the film after changing the gas in the cell. Initial calibration of the SPEX spectrometer was also performed.

To support initial low temperature (<120 °C) tests of the cell, we investigated several simple methods for immobilization of $\text{Mo}_6\text{Cl}_{12}$ onto substrates. Two different approaches were investigated. In the first, we used a thin layer of polyethylene as a binder for immobilizing $\text{Mo}_6\text{Cl}_{12}$ on the surface of a quartz substrate. We observed poor adhesion of the binder to the quartz substrate at low temperatures and a reduced sensitivity to oxygen. The latter indicates that the binder had encapsulated the clusters, reducing the permeability of oxygen, oxygen and severely limited quenching of the luminescence. In a second approach, we prepared a concentrated solution of the acetonitrile complex of $\text{Mo}_6\text{Cl}_{12}$ and evaporated the viscous solution to dryness. This simple technique gave immobilized clusters that strongly adhere to the surface. Since the initial films were relatively thick, we are currently developing protocols that will reliably yield thin films with predictable photophysical properties. We are concurrently pursuing the use of a sol gel matrix for operation at high temperatures.

EXPERIMENTAL

Synthesis

Molybdenum chloride (0.5073g, 3.04mmol) from Cerac was dissolved in 6M HCl with heating to form a clear yellow solution. The volume was then reduced to $\frac{1}{4}$ and allowed to cool to room temperature. After placing the flask in a freezer overnight, long yellow needle-like crystals were obtained. The solution was decanted from the flask and the crystals were collected, broken into smaller needles to facilitate drying, and dried on a piece of filter paper. Once dry, $\sim 1/2$ half of the crystals were set aside for future analysis, and the remaining crystals were transferred to a Schlenk tube and heated under vacuum at 150 °C for 2.5 hours. After 2.5 hours, the temperature was increased to 204 °C for 12 hours to obtain an orange-yellow powder.

Fluorescence

Thin film samples were prepared on substrates cleaned by rinsing with menthol, drying in an oven for 30 minutes, and then placing them into a UVP PR-100 uv-ozone reactor for 30 minutes. Samples for fluorescence measurements were prepared by placing a small polyethylene strip across the substrate and heating until melted (120 °C). Powdered $\text{Mo}_6\text{Cl}_{12}$ was evenly distributed on the film and rolled flat using the edge of a Pasteur pipette, and the excess $\text{Mo}_6\text{Cl}_{12}$ was then removed. Polyethylene-free films on quartz were prepared by concentrating a solution of the acetonitrile complex of $\text{Mo}_6\text{Cl}_{12}$ to an oily consistency, and then applying the solution to the quartz surface using a pipette. Evaporating to dryness overnight gave yellow films that strongly adhered to the surface.

The fluorescence measurements were performed using a Fluorolog-3 instrument from Instruments S.A., Inc. The system includes a single Czerny-Turner excitation spectrometer with a 1200g/mm ruled grating blazed at 330nm and a single Czerny-Turner emission spectrometer with a 1200g/mm holographic grating blazed at 630 nm. The excitation optics consists of a 450W ozone free Xe lamp, followed by a 270-380 nm bandpass filter (Oriel 1124). A Si photodiode is used to continuously monitor the lamp signal. The detection optics consists of 603.2 nm long wave pass filter (CVI) followed by a multi-alkali photo multiplier tube (Hamamatsu R928) with photon counting electronics. Data processing was performed using the Datamax (version 2.2) software package supplied with the instrument. Spectra were obtained by exciting at 313 nm or 436 nm and scanning the emission monochromatic from 500 to 1000 nm, or 550 to 850 nm.

Measurements of the cluster fluorescence in solution with different concentrations of dissolved oxygen were performed by placing the solution in a quartz cuvette sealed with an airtight septum. Nitrogen gas of purity 99.999% was bubbled through the solution for 10 minutes to obtain the measurements in a 0.001% oxygen environment. The atmosphere measurements ($\sim 20\%$ oxygen) were performed after removing the septum, pipetting the solution several times in and out of the cuvette and allowing the solution to stand for 2 hours.

X-ray powder diffraction

Samples were prepared by first placing a small piece of double sided tape on top of a microscope slide. Using a spatula, a small amount of powdered sample was then placed on top of the tape and spread around to evenly distribute. Once spread evenly, the powder was pressed gently to insure that the sample was stuck to the tape. The microscope slide was gently tapped on its side to dislodge loose powder that might get into the goniometer.

Microscopy

Polarized optical microscopy images were acquired using a Nikon Optiphot2-Pol equipped with a Sony Hyper HAD CCD-IRIS/RGB color video camera (model DXC-151A). The camera was connected to a PC using a Sony camera adapter (model CMA-D2). The images were viewed using a Sony Trinitron color video monitor. Images were taken using Hauppauge computer works Win/TV software (version 2.4.17052). Images collected at 0 and 90° to characterize the birefringence of the samples and a qualitative measure of their degree of crystallinity.

Microwelding for construction of the Pt heater assembly

A parallel gap resistance micro-joining technique, using a Unibond II system from Unitek Equipment, was used to attach the electrical buses for the Pt heater assembly. The copper electrodes had a fixed 0.15 mm electrode spacing, the system was operated in feedback mode with the force set at 200 units and a welding time of 39 ms. The welding parameters for the two different Pt wire combinations were:

Pt (0.09 mm) to Pt (0.125 mm) – 1.2 V applied bias

Pt (0.125 mm) to Pt (0.25 mm) – 1.1 v applied bias

RESULTS AND DISCUSSION

Emission

Figure 1 shows the emission spectra for freshly synthesized and previously synthesized $\text{Mo}_6\text{Cl}_{12}$ [2], both taken on our current spectrometer. The similarity between the line shape of the two spectra indicates that the photophysical properties of our current material and that synthesized by Newsham are similar. Note however that these spectra were obtained before the spectrometer's emission monochromator had been properly calibrated, resulting in a mis-calibration of the wavelength axis.

Following these initial measurements a number of steps were taken to significantly improve the performance of the Fluorolog spectrometer. The excitation spectrometer was calibrated in the near UV using the 467 Xe line and a Hg standard lamp was been purchased to obtain an additional calibration wavelength at 313 nm. The emission spectrometer was calibrated using the water Raman peak at 397 nm. A Neon standard lamp with sharp lines in the wavelength of interest, 600-800 nm has been obtained and is in the process of being implemented. The spectral response functions of the 330 nm excitation grating and the 630 nm emission grating were obtained and implemented into the data analysis software.

Shown in Figure 2 are the emission spectra for our freshly synthesized $\text{Mo}_6\text{Cl}_{12}$ dissolved in methanol, under atmospheric conditions (~20% oxygen) and in a 0.001% oxygen (balance gas is nitrogen) obtained following the calibration procedure described above. Comparison with previously published data of the molybdenum clusters in MeOH (shown in Fig. 3) indicates that we are obtaining the correct lineshape. Figure 2 also demonstrates that our molybdenum clusters are sensitive to the concentration of oxygen in solution, a quenching of a factor of three was observed upon changing the oxygen concentration from 0.001% to ~20%. We had previously obtained a quenching of a

Figure 1. Fluorescence measurements at room temperature for a) current $\text{Mo}_6\text{Cl}_{12}$ in MeOH, b) previously synthesized $\text{Mo}_6\text{Cl}_{12}$ in methanol.

factor of 5.5 in thin film samples [4] and are investigating the possible sources of the discrepancy.

Figure 2. Emission spectra of freshly synthesized $\text{Mo}_6\text{Cl}_{12}$ clusters in methanol (conc. = 0.15 g/L) demonstrating quenching by oxygen. The pump wavelength is 313 nm. Nitrogen: 99.999%; Oxygen: ambient air.

Figure 3. Emission spectra [2] at room temperature of (—) Mo_6X_{12} in MeOH; (---) $\text{Mo}_6\text{Cl}_{12}$ in silicon-oxide gel; (···) $\text{Mo}_6\text{Br}_{12}(\text{OSi}(\text{CH}_3)_3)_2^{2-}$ in MeOH.

X-ray Powder diffraction and Microscopy

The results of the x-ray powder diffraction before and after heating, figure 4, indicate a substantial loss in crystallinity after heating. The loss in crystallinity is attributed to disorder imposed by the loss in of HCl from the crystal lattice. The loss is between cluster crystals, not within them, and this has no effect on the photophysical properties. This is the reason that we saw the correct absorption and emission data, but the compound appeared amorphous. X-ray powder diffraction gives results for both long and short-range order, but the results are a linear combination. The net effect on our material after heating was an amorphous appearance.

Figure 4. X-ray powder diffraction patterns of $\text{Mo}_6\text{Cl}_{12}$ before and after heating.

Figure 5. Polarizing optical microscopy of $\text{Mo}_6\text{Cl}_{12}$
a) initial position b) after 90° rotation.

Platinum heater assembly

The photophysical parameters of thin films of the molybdenum clusters as a function of temperature and oxygen concentration will be obtained using the quartz cell described in the previous report. Thin films of the clusters will be deposited on an oxidized silicon substrate with an array of Pt heaters glued to the backside of the sample. Shown in Figures 6a and 6b are optical images of the back and front view of the assembled three heater array. Each heater has two Pt legs (0.09 mm) which are attached to either the positive or negative voltage bus (Pt 0.25 mm). The heaters are wired in parallel to insure uniform distribution of power in the silicon substrate. Construction of the array was complicated due to the small diameter of the leads and the need to make precise electrical contacts without shorts. A resistance microwelder with micro-positioning capabilities was used to weld the Pt heater legs to the Pt voltage bus as shown in the picture and silica braided sleeving for insulation. This type of microwelder is not available at Michigan State, we used an instrument belonging to colleagues at the Ford research laboratory. Our future work will require purchasing a microwelder.

Figure 6a. Optical image of an array of three platinum heaters (back view) that will be used to heat the cluster thin films in the quartz cell.

Figure 6b. Front view of array of three platinum heaters.

CONCLUSIONS

The $\text{Mo}_6\text{Cl}_{12}$ synthesized by us is the correct compound. Long-range order in the hydrochloride salt is lost upon heating, giving rise to an amorphous x-ray scattering pattern. Because the structure of the individual clusters determines the photophysical properties of $\text{Mo}_6\text{Cl}_{12}$, the loss in long-range order will not have an effect on the absorption and emission of the clusters. Emission results from solid $\text{Mo}_6\text{Cl}_{12}$ in air and under nitrogen indicate that we have that material needed for our experiments. The quartz cell positioning system has been modified and a heater assembly for high temperature thin film measurements was developed.

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None.

LIST OF ACRONYMS AND ABBREVIATIONS

HCl – Hydrochloric Acid

MeOH – Methanol

CH_3CN – Acetonitrile