Fiber Optical Micro-detectors for Oxygen Sensing in Power Plants

Quarterly Technical Report
Reporting Period:
April 1, 2004 to June 30, 2004

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July 2004

DOE Award Number: DE-FC26-02NT41582

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ABSTRACT

A reflection mode fiber optic oxygen sensor that can operate at high temperatures for power plant applications is being developed. The sensor is based on the $^3O_2$ quenching of the red emission from hexanuclear molybdenum chloride clusters. Alkali salts of Mo_6Cl_{12} were synthesized and heated to 280 °C for one hour in air. Optical measurements of the thermally treated material confirm the potential of the salts as lumophores in high temperature fiber optic sensors. In addition sol-gel films containing Mo_6Cl_{12} were dip coated on quartz substrates and heated at 200 °C for one hour. Conditions were developed for successfully immobilizing monomeric complexes that are compatible with sol-gel processing.

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INTRODUCTION

Maximizing the efficiency of combustion processes 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 Mo_6Cl_{12}-based clusters relevant to this project. Mussell described the synthesis of the molybdenum clusters, and Newsham gives a good account of the properties of neutral Mo_6Cl_{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 Mo_6Cl_{12}, Ruud dispersed Mo_6Cl_{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 demonstrated a fast room temperature fiber optic sensor based on oxygen quenching of the luminescence from the PTMSP/Mo_6Cl_{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. With these facts in hand, we anticipate promising results from our design.

EXECUTIVE SUMMARY

Previously, we successfully immobilized Mo_6Cl_{12} in a porous sol-gel film, thus accomplishing a critical step towards the development of an inorganic fiber optic oxygen sensor for high temperature applications. High temperature stability issues were addressed by characterizing by depositing thin sol-gel films deposited on planar fused silica substrates and measuring quenching of the red luminescence following temperature cycling to 200°C. Appropriate conditions for immobilizing monomeric complexes of Mo_6Cl_{12} that are compatible with sol-gel process were developed. Earlier thermal stability tests showed that Mo_6Cl_{12} degraded in air at T >250 °C. X-ray diffraction measurements on samples annealed at 300 °C under controlled conditions have allowed us to determine the principal degradation products.

We synthesized alkali salts of Mo_6Cl_{12} and found that they are more stable than that of the parent compound. Optical experiments show that after heat cycling to 280 °C, the luminescence line-shape of the salts are identical to that of Mo_6Cl_{12} that have not been heated. In addition oxygen quenching of the thermally cycled films was observed. Experiments are underway to improve the purity of the salts.

A sample cell for performing spectroscopy of the Mo_6Cl_{12} clusters and/or cluster/sol-gel films up to 200 ºC was developed. Measurements are presented for the Mo-cluster / sol-gel composite film as a function of heater temperature.

EXPERIMENTAL

Materials.

All glassware was oven-dried prior to use. Acetonitrile (Spectrum Chemical Company, HPLC grade) was dried over CaH_2 and distilled prior to use. Tetraethyl orthosilicate (TEOS) (Aldrich, 98%) and hydrochloric acid (CCI, electronics grade) were used as received. Molybdenum dichloride (Cerac, Inc.) was purified as described elsewhere [12]. Suprasil – W1 quartz microscope slides (3" × 1" × 1 mm) were obtained from Heraeus Amersil and were cut into 1.25 cm × 2.45 cm pieces. Slides were handled with gloves and tweezers in order to minimize surface contamination and then washed with Alconox, rinsed with distilled water, soaked in a base bath (~5M NaOH in 95% ethanol), rinsed with distilled water, and stored in distilled water until use.

Optical characterization of films.

Absorption spectra were measured using a Perkin-Elmer Lambda 40 series double beam UV/vis spectrometer. Data analysis was performed using the UV Win lab (version 2.80.03) software package supplied with the instrument. Fluorescence measurements were performed using a Fluorolog-3 instrument from Instruments S.A., Inc. The excitation optics consisted of a 450W Xe lamp, followed by a 330 nm ruled grating and a 270-380 nm bandpass filter (Oriel 1124) to remove undesired Xe lines. The detection optics consisted of a 600 nm long wave pass filter (CVI) followed by a 630 nm holographic grating and multi-alkali photo multiplier tube at 950V (Hamamatsu R928). Data processing was performed using the Datamax (version 2.2) software package supplied with the instrument. The excitation beam was centered at 313 nm with a 5 nm bandpass and the emission monochromator was scanned from 550 to 850 nm in 1nm steps. The emission spectra have been corrected for both the spectral response of the 630 nm emission grating and the photo multiplier tube.

Measurements of cluster fluorescence in solution were performed by placing the solution in a quartz cuvette sealed with an airtight septum. Spectra were measured in laboratory air and high purity nitrogen (AGA, Inc, 99.999%). Prior to obtaining spectra, all gases were bubbled through the solution for 10 to 15 minutes at a rate of ~10 mL / min. via a glass pipette inserted through the septum. For the measurements of the salts in HCl a glass pipette was used to bubble oxygen into the solution. Measurements of the sol-gel immobilized clusters were made in the same manner. The film-coated side of the quartz slide was irradiated at an angle of ~40º with a 90º angle maintained between the excitation beam and detector. The slides were purged in-situ and care was taken not move the excitation spot between measurements in the different gas environments.

X-ray powder diffraction

Samples were prepared by using a spatula to evenly distribute a small amount of powdered sample on double-sided tape mounted on a microscope slide. After pressing gently to insure that the sample adhered to the tape, the microscope slide was gently tapped on its side to dislodge any loose powder.

RESULTS AND DISCUSSION

Immobilization of Mo_6Cl_{12} in sol-gel matrices

Developing a high temperature oxygen fiber sensor based on requires a scheme for embedding the clusters in a matrix while retaining their unique optical properties. In addition, the matrix must have high oxygen permeability and adhere strongly to the optical fiber. These requirements can be satisfied by using a sol-gel matrix to immobilize the clusters at the tip of high temperature silica fibers, such as a commercially available gold clad silica fiber rated for long term operation up to 750 °C [13]. The silanol terminated surface of the fiber ensures excellent adhesion to the matrix, and prior work has shown that the oxygen permeability of sol-gel matrices can be tailored by appropriate choice of reaction conditions.

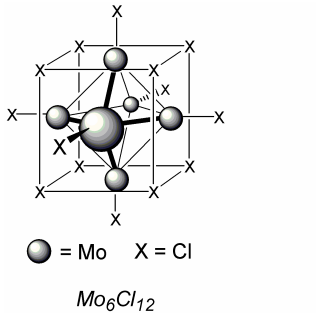

Figure 1. Luminescent molybdenum clusters.

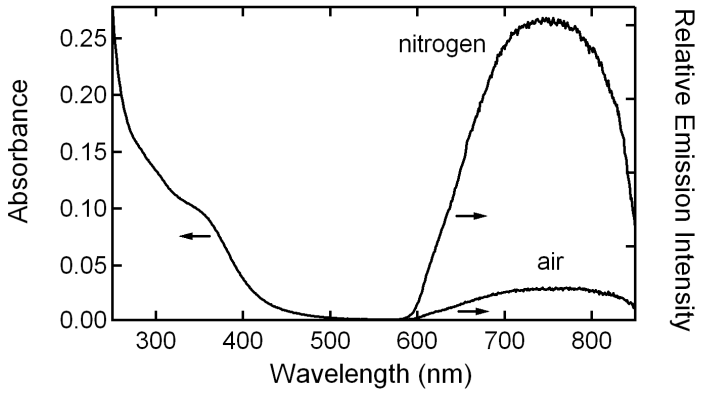

Figure 5. Absorption and emission spectra of Mo_6Cl_{12} in acetonitrile. The cluster concentration is 4×10^{-5} M. The emission spectra demonstrate oxygen quenching by a factor of 9.6 between (a) nitrogen (99.999%) and (b) laboratory air (~20% oxygen).

The spectroscopic features of the cluster in acetonitrile are shown in ***Figure2***. Excitation of Mo_6Cl_{12} clusters in the UV (λ<400 nm) leads to a long lived triplet state, which decays to the ground state with emission of red luminescence centered at ~750 nm. The large Stokes shift of the emission (> 300 nm) greatly simplifies the design of a reflection mode fiber sensor since photons over the entire emission band can be collected and the UV

pump signal can be removed using simple band pass filters. In addition, the near unity quantum yield allows simple sources such as mercury pen lamps to be used as the UV source. Excitation spectra were obtained by pumping at 313 nm while scanning the emission from 550 to 850 nm.

The excited states of Mo_6Cl_{12} clusters are efficiently quenched by oxygen. Spectra for Mo_6Cl_{12} in solution measured in room air and under nitrogen are shown in ***Figure 2***. The data show a quenching factor of 9.6, with the luminescence intensity and lineshape returning to their original values upon equilibration with room air. Luminescence quenching data for Mo_6Cl_{12} clusters typically follows the Stern-Volmer equation, $I/I_0 = 1/(1+K_{sv}[O_2])$, where I and I_0 are the luminescence intensity in the presence and absence of oxygen of concentration $[O_2]$ and K_{sv} is the Stern-Volmer constant [5].

Measurement of Mo_6Cl_{12} luminescence as a function of temperature.

The luminescence of Mo-cluster/sol-gel film 15F was measured as a function of temperature in flowing N_2 (purity 99.999%). Shown in ***Figure 3*** is the integrated signal intensity (i.e. integrating all the luminescent photons in the 580-850 nm emission bandwidth of Fig. 2) of the sample as a function of heater temperature. The luminescence signal decreases with increasing temperature, as observed previously in the 1.4 to 300 K regime [18]. No temperature dependent hysterisis was observed. . Note that the temperature scale in ***Figure3*** is that of the platinum heater glued to the back of the quartz substrate. We estimate that the temperature of the Mo-cluster / sol-gel film itself is a most 30 °C lower than the heater temperature. Experiments are currently under way to measure the sol-gel film temperature as a function of heater power using a 100 ohm Pt solid state thermometer. Measurements of the degree of oxygen quenching as a function of temperature are in progress.

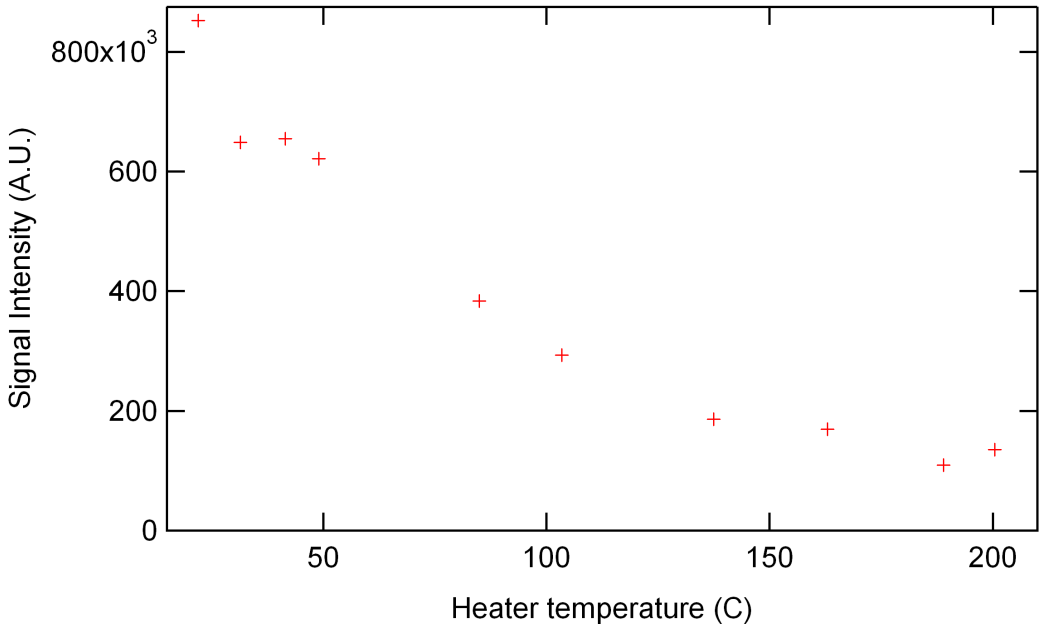

Figure 3 Integrated luminescence intensity (580 - 850 nm) of Mo-cluster / sol-gel composite film 15F as a function of heater temperature. The measurements were taken in flowing nitrogen (99.999%).

We estimate that the UV power density of the excitation source at our sample is about 1 mW/cm^2. Our previous room temperature fiber sensor measurements [5] were made with an incident power density of 9 mW/cm^2, and the cross sectional area of the fiber sensor was roughly a factor 10 smaller than the illumination spot during our current measurements. From the signal to noise in the measurements shown in ***Figure3*** we anticipate that despite the decrease in the integrated signal intensity with temperature, we will have enough luminescent photons to develop a fiber optic based sensor using Mo-cluster / sol-gel composite films similar to that of sample 15F. We will investigate increasing the cluster concentration and/or making thicker films to increase the signal if that proves to be necessary.

CONCLUSIONS

We have developed a scheme for embedding luminescent hexanuclear molybdenum chloride clusters in sol-gel matrices Spectroscopic measurements show that the photophysics of the clusters are unchanged by the immobilization process. An experimental setup was developed for in-situ measurements of the cluster/sol-gel composite films as a function of temperature. After heating the cluster/sol-gel composite to 200 °C, oxygen quenching of the cluster luminescence was preserved. These results provide a route for development of a silica fiber based high temperature oxygen sensor.

An alkali salt of Mo_6Cl_{12} were synthesized and heated to 280 °C for one hour in air. Absorption and luminescence measurements confirm the potential of the salts as lumophores in high temperature fiber optic sensors. Slight differences in the intensity and shape of the absorption spectra of thermally aged salts and solutions of Mo_6Cl_{12} suggest the presence of Mo_6Cl_{12} as a minor impurity in the as-synthesized the salt, which oxidizes upon heated to 280 °C.

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BIBLIOGRAPHY

None.

LIST OF ACRONYMS AND ABBREVIATIONS

HCl – Hydrochloric Acid
MeOH – Methanol
TEOS – Tetraethyl orthosilicate