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*Invited Paper

OXOMETALATE-GLASS COMPOSITES AND THIN FILMS

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ABSTRACT

New glass-composites with ion exchange properties have been developed. Ammonium 12-molybdophosphate (AMP) $(NH_4)_3PMo_{12}O_{40}$, and ammonium 12-tungstophosphate (AWP) $(NH_4)_3PW_{12}O_{40}$, known for their ion exchange capabilities, are included either in preformed aerogels with defined pore size, or are added to sol-gel mixtures during the process of gel formation. Characterization is carried out by FTIR, Raman and EXAFS spectroscopy. Ion exchange capacities for the oxometalate precursors are determined for silver and rubidium and are compared to those of the glass composites. Glass composites show high ion exchange capacity, but some portion of the metalate complexes leaches from the glass during the procedure. This is in contrast to thin composite films, which have almost no porosity and do not show loss of metalate. EXAFS spectroscopy demostrates that the oxometalate microstructure is maintained in glass composites and that rubidium ions after ion exchange in glasses occupy similar cation positions as in the precursor compounds.

INTRODUCTION

The combination of different functional properties in glass-based composites offers great potential for the design of tailored materials. Examples include sol-gel derived glass-organic composites, glass-included laser dyes, catalysts, and nonlinear optical materials.

In view of the increasing demand for stable, ion-selective sensors we have initiated a program aimed at the design of tailored thin films with selective ion exchange capabilities. In combination with highly sensitive acoustic devices, it is envisioned that inexpensive, rugged ion sensors for process and environmental monitoring can be designed. The concept is based upon the encapsulation of oxometalate clusters in porous, sol-gel derived glasses. The resulting materials combine selective ion exchange sites with tailored porosity, such that ultimately large fractions of unwanted species (e.g., organics, biological matter) are screened from the ion exchange sites. The following benefits are expected from this approach: The design of *ion exchange composites* allows independent adjustment of both ion selectivity through the choice of different oxometalates, and porosity through the choice of sol-gel chemistry. Furthermore, the resulting inorganic films are temperature stable up to at least 300°C and not subject to fouling.

Heteropoly oxometalates such as anions with the Keggin structure are known since the last century, but their crystal structure was first solved by Keggin in 1934. Figure 1 depicts the Keggin anion structure and a defect structure with one MO_6 octahedron missing. These materials find numerous applications in catalysis, analytical chemistry and biochemical or medical areas. Their ability to exchange their counter cation for alkali ions was first recognized by Smit[1] and has since been used in column chromatography and in paper chromatography. Keggin ions have been used to exchange alkali cations as well as radioactive pollutants. General reviews are available.[2,3,4,5]

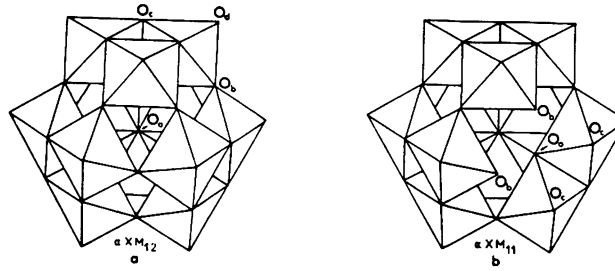

Figure 1: Idealized Keggin structure XM_{12} (a) and defect Keggin structure XM_{11} (b). The central XO_4 tetrahedron is not shown. O_a = oxygen shared by 3 MO_6 and the central XO_4 tetrahedron, O_b and O_c = oxygen shared by corner and edge linked MO_6, O_d = terminal unshared oxygen

This communication reports on the design of 12-molybdophosphate and 12-tungstophosphate ions encapsulated in silicate glass bodies in bulk form. FTIR, FT-Raman, EXAFS, and ion exchange data demonstrate the feasibility of creating intact intra-glass oxometalate ions that are accessible for ion exchange through the pore system of the matrix.

EXPERIMENTAL:

1. Sample Preparation

a) Ammonium 12-molybdophosphate (AMP) $(NH_4)_3PMo_{12}O_{40}$. Highest yield (82 - 95% after work-up) is obtained by stepwise combining stoichiometric amounts of Na_2MoO_4, H_3PO_4, and NH_4NO_3 (in 0.1 M HNO_3) under acid conditions. 1 molar aqueous solutions were added in a volume ratio 12:1:3 after acidifying the sodium molybdate solution with 13 M HNO_3 to pH 1.6. The slightly yellow color of the molybdate turned to strong yellow immediately after addition of phosphoric acid. Precipitation of the ammonium salt occured promptly.

b) Ammonium 12-phosphotungstate (AWP) $(NH_4)_3PW_{12}O_{40}$. Sodium tungstate is insoluble in acid solutions and forms a thick white precipitate when acidified with HNO_3. Thus, 10 ml WO_4^{2-} and 0.9 ml 1 M NaOH and 0.9 ml of 1 M H_3PO_4 are combined, followed by addition of 2.5 ml NH_4NO_3 at pH 7 and acidification to pH 1.5. AWP precipitates as a white solid (yield 92%). The corresponding white silver salt is prepared by adding $AgNO_3$ before acidification (Yield 50%).

c) Assembly of AMP within pores of aerogels. To a slurry of 1g TEOS-derived B2-Aerogel (pore size 10-500 Å) in 10 ml H_2O, 4 ml of 1 M Na_2MoO_4 and 2 ml of 13 M HNO_3 are added. The slurry is stirred for 10 minutes before adding 0.33 ml of 1 M H_3PO_4, and finally, 1 ml of 1 M NH_4NO_3. A green color resulting from reduction of the AMP was reversed to yellow upon adding 2 ml 30% H_2O_2. After filtration the yellow solid was dried at 85°C.

d) Preparation of glasses containing oxometalates

HMP-Glass. 3 g of crystalline 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$; HMP) and 7.3 ml EtOH and 1 ml 0.1 M HNO_3 and 7.3 ml TEOS and 2 ml 0.05 M NaOH are combined in this sequence (molar ratio of HMP:SiO_2 = 1:20). The suspension was sonicated for 3 minutes and left at room temperature. After two days a greenish gel had formed.

AMP-Glass. Synthetic AMP + TEOS + EtOH in a molar ratio of AMP:SiO_2 = 1:20: Stoichiometric amounts of 1 M Na_2MoO_4 (40 ml) and 1 M H_3PO_4 (3.33 ml) solutions (at pH = 1.5, 6 ml 13 M HNO_3) were combined. Water was evaporated at 75 C to about half the volume (25 ml) until a yellow cloudiness indicated the starting point for precipitation. 14.6 ml TEOS were added to the warm, clear solution under strong stirring, and immediately stoichiometric amounts of NH_4NO_3 in ethanol were added (1.1 g in 1 ml 0.1 M HNO_3 plus 14.6 ml EtOH). A cloudy yellow color appeared. Stirring was continued under slow cooling of the slurry. A thick paste was formed after 2 hours. After 1 day ethanol was partially removed by heating in a water bath. A hard, yellow glass formed.

2. Characterization

Metal contents of glasses were determined by atomic absorption. The samples were analyzed as-synthesized and after each subsequent treatment by FT-IR in the form of KBr pellets. For FT-Raman experiments, a Spectrum SL301 Nd:YAG laser (1064 nm, ca. 1.0 W) was focused on a 1-mm capillary containing the powdered sample. Light collection was done with a modified Mattson Polaris interferometer, detection with an InGaAs detector (EPITAXX). EXAFS measurements were peformed at the X-11A beamline at NSLS (Brookhaven National Laboratories) with an electron energy of 2.5 GeV and ring currents between 90 and 180 mA. Data were collected with a Si(400) crystal pair monochromator at the Mo K-edge (20,000 eV) and at the W L_{III}-edge (10,207 eV) at ca. 100 K. Rubidium-exchanged samples were also examined at the Rb K edge (15,200 eV). Data analysis was performed following standard procedures.[6]

3. Ion exchange

Ion exchange was performed on bulk oxometalates as well as on glass composites by adding stoichiometric or excess amounts of $AgNO_3$ or $RbNO_3$ in acid solutions (e.g., 500 mg AWP and 50 ml of 0.01 M $RbNO_3$ in 0.1 M HNO_3). Samples were stirred for ca. two hours in exchange solutions, filtered and further analyzed. Back-exchange capabilities were examined on bulk oxometalates by adding varying amounts of NH_4NO_3 in acid solution.

RESULTS AND DISCUSSION

Bulk oxometalates

Characteristic modes of the M-O and P-O vibrations appear between 200 and 1100 cm^{-1} in the IR and Raman spectra. The main IR vibrations at 1064, 964, 875, 795 and 595 cm^{-1} of the molybdate ions, or, 1081, 990/982, 890, 805 and 535 cm^{-1} of the tungstate ions are assigned as the asymmetric P-O, M-O_d (O_d = terminal oxygens), and M-O-M vibrations according to Rocchiccioli-Deltcheff.[7] Raman spectra show mainly the symmetric M-O_d band around 1000 cm^{-1} and a convolution of the symmetric P-O and asymmetric M-O_d band around 990 cm^{-1}.

Inclusion of Keggin ions in preformed aerogel

The preparation of oxometalates in preformed glasses resulted in a loading of ca. 8 wt% Mo in B2-aerogel and a yellow color indicated formation of AMP. The IR spectrum is shown in Figure 2. The silica support blocks out a region between 1350 and ca. 1000 $cm^{-1}$and obscures an even wider range in the IR. However, the main bands of the Keggin ions (1064, 970, 875, 795 cm^{-1}) are still visible as superimposed peaks when compared with the precursor included in the Figure.

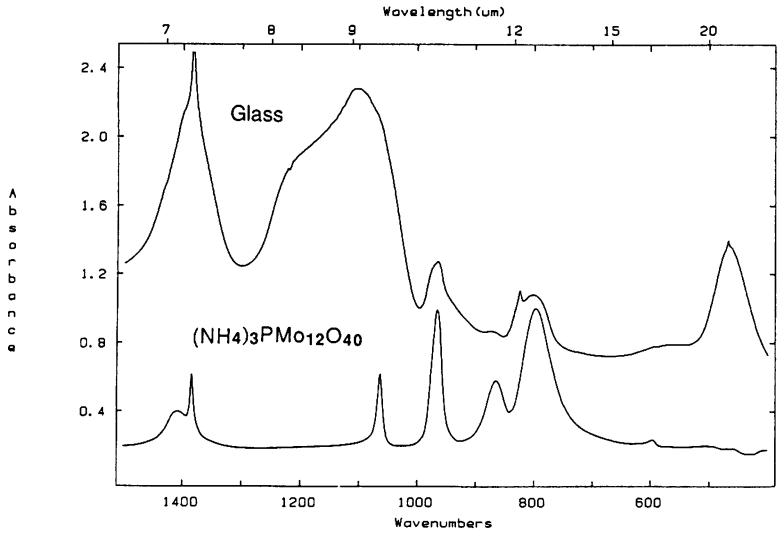

Figure 2: FTIR spectrum of the preformed aerogel with included $(NH_4)_3PMoO_{40}$ in comparison to the precursor

When a part of this sample was washed with a small amount of water at room temperature, the color changed from yellow to white and no Keggin ions were detectable in the solid. Heat treatment in air up to 200 C was thought to favour condensation reactions between the aerogel and the Keggin ions. A similar washing procedure as above still reduced the molybdenum content, but left ca. 50% attached to the solid. After a subsequent ion-exchange experiment with silver nitrate, all remaining molybdenum ions were found in the wash solution.

Inclusion of Keggin ions during gellation

To avoid or reduce the loss of molybdenum from supported samples upon washing, a different strategy for encapsulation of Keggin ions was developed: Oxometalate complexes were synthesized in the presence of sol-gel precursors for the silicate matrix. It was anticipated that bottleneck pores develope which restrict mobility of the Keggin ions but render access for smaller cations. Several different glasses were prepared varying in the sol-gel route and/or the Keggin ion present. A representative IR spectrum is shown in Figure 3 (AMP in TEOS + EtOH). The high loading of ca. 38 wt% of Mo allows for ready detection of the Keggin vibrations which confirm that the Keggin structure is maintained in the glass. The thermal stability of this glass was tested by heating up to 400 ^{0} C in oxgen. Raman spectra of a representative experiment are shown in Figure 4. It is clearly visible that decomposition occurs between 200 and 400 ^{0} C. Aging temperatures were therefore restricted to 200 ^{0} C.

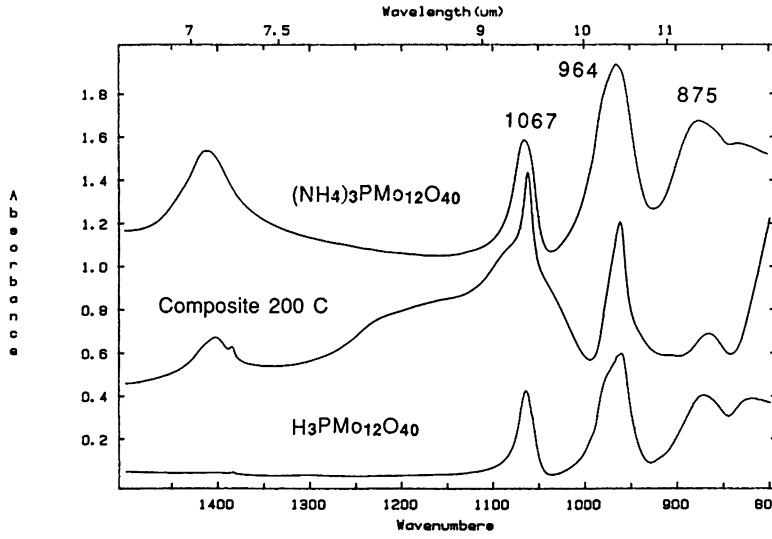

Figure 3: FTIR spectra of "In-situ" formed composite TEOS + EtOH + $(NH_4)_3PMoO_{40}$ in comparison to the precursor $(NH_4)_3PMoO_{40}$ and H_3PMoO_{40}

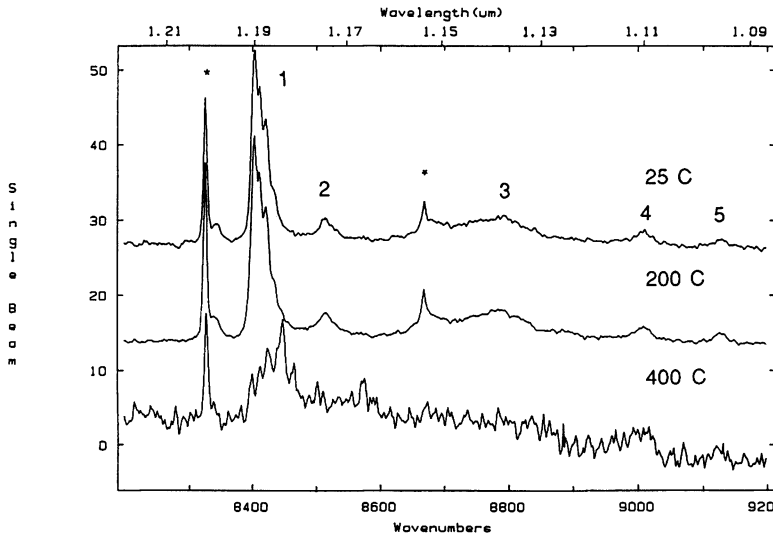

Figure 4: FT-Raman spectra of the thermal degradation of "In-situ" formed composite TEOS + EtOH + $(NH_4)_3PMoO_{40}$. Wavenumbers are given (the laser line is at 9388 cm^{-1}). Stokes shifts are as follows (subscripts see Figure 1[9]):

(1) 989 cm^{-1}: Mo-O_d symmetric stretch
(2) 879 cm^{-1}: Mo-O_b-Mo asymmetric stretch
(3) 600 cm^{-1}: Mo-O_c-Mo symmetric stretch
(4) 381 cm^{-1}: Mo-O-Mo bending
(5) 250 cm^{-1}: Mo-O_a-Mo symmetric stretch
* : NO_3^-

Ion exchange

The bulk oxometalates were ion exchanged with rubidium and silver by offering stoichiometric amounts of the cations at room temperature. AMP, AWP and the respective silver salt exchange under these conditions 50% of their cations for rubudium, while AMP and AWP exchanged only 12-15 % of their ammonium ions for silver. However, a 100% exchange is achieved upon offering excess of silver nitrate.

When silver salts of the molybdenum and tungsten Keggin ions were exposed to ammonium ions, back-exchange to the ammonium form occured for AgMP up to 92% and for AgWP up to 54% in a 3 M NH_4NO_3 solution.

The glass composites exchanged larger fractions of their protons or ammonium cations, e.g., 12 - 76% for Ag and 42 - 92% for Rb. However, some leaching of the oxometalates was observed for all different porous glasses. Composites made with TEOS showed a loss of 30 - 58% Mo or W, while glasses made from A2 solutions (TEOS + EtOH refluxed at 60 C for several hours) showed a loss from 16 - 35 %. The preformed aerogel lost up to 98% after two successive exchange cycles. The loss of Keggin ions is effectively suppressed in thin films of similar compositions which were found to be non-porous. Multicomponent glasses which retain porosity even in thin films are presently studied.

EXAFS analysis

EXAFS measurements were performed on the bulk oxometalates as well as on glass composites before and after ion exchange. EXAFS allows to determine the local structure around the X-ray absorbing atom of choice and can provide detailed information about bond distances, coordination numbers and types of atoms in the nearest neighbor shells. Figure 5 shows Fourier transformed molybdenum EXAFS data of the precursors AMP and HMP, overlayed with the respective composites formed with these Keggin ions. A large peak indicating the oxygen environment of the molybdenum atoms is visible between 0.5 and 2 Å (Bond distances appear at ca. 0.5 Å to lower bond distances due to phase shift effects). The mean bond distances obtained from X-ray diffraction are 1.70 Å for the terminal oxygens, 1.92 Å for oxygens bridging the molybdenum octahedra, and 2.43 Å for the oxygen linked to the central phosphorus atom. The second and third shells arise from Mo-Mo bonds at 3.42 Å from edge-shared octahedra and at 3.70 Å from corner-shared octahedra. It can clearly be seen that precursor and glass composites have the same local structure. A quantitaitve analysis of these data is in progress.

When a HMP/TEOS composite is analyzed after rubidium exchange, the Mo-edge EXAFS data do not show any sign of degradation (see Figure 6; the imaginary parts of the Fourier transformations are shown in addition to the magnitudes. The former give valuable information about the nature of neighbors or overlap of peaks). The rubidium edge data show a large contribution around 2.5 Å (uncorrected for phase shift) which indicates a Rb-O interaction, while the peak around 3.9 Å arises from the Rb-Mo bond. This spectrum is identical to that taken from the bulk rubidium phospho molybdate and indicates that the rubidium ions occupy identical cation positions in both compounds. When fitted with adequate reference compounds a bond distance of ca. 4.4 Å can be expected. To our knowledge the only complete determination for cation positions in Keggin ions is done with combined neutron- and X-ray diffraction by Brown et al.[8] Their distance of hydrated protons to molybdenum atoms agrees closely with the above observations.

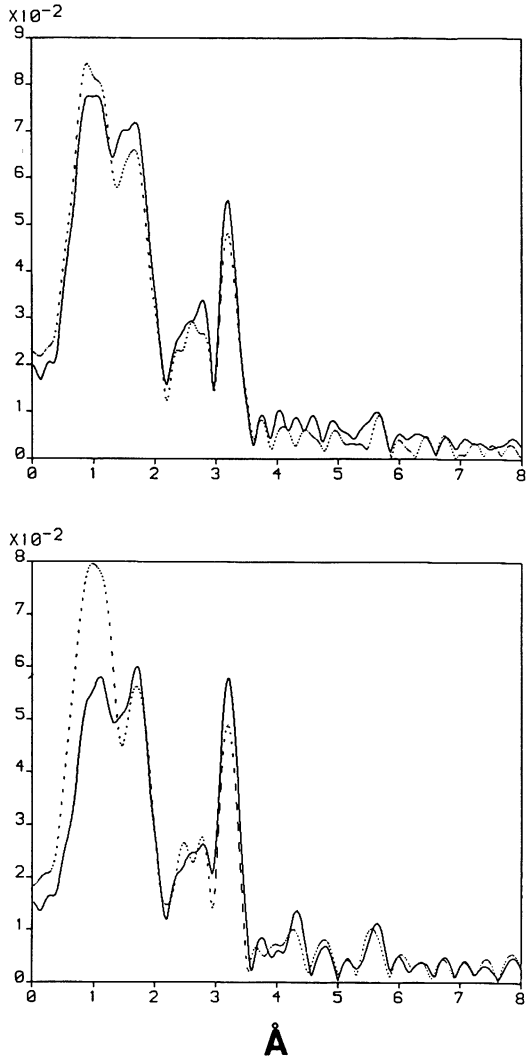

Figure 5: Molybdenum EXAFS data: top: Fourier transformation of the precursor $(NH_4)_3PMo_{12}O_{40}$ data (solid line) as compared to the aerogel composite broken ine). Bottom: Fourier transformation of the precursor $H_3PMo_{12}O_{40}$ data (solid line) as compared to the TEOS composite (broken line)

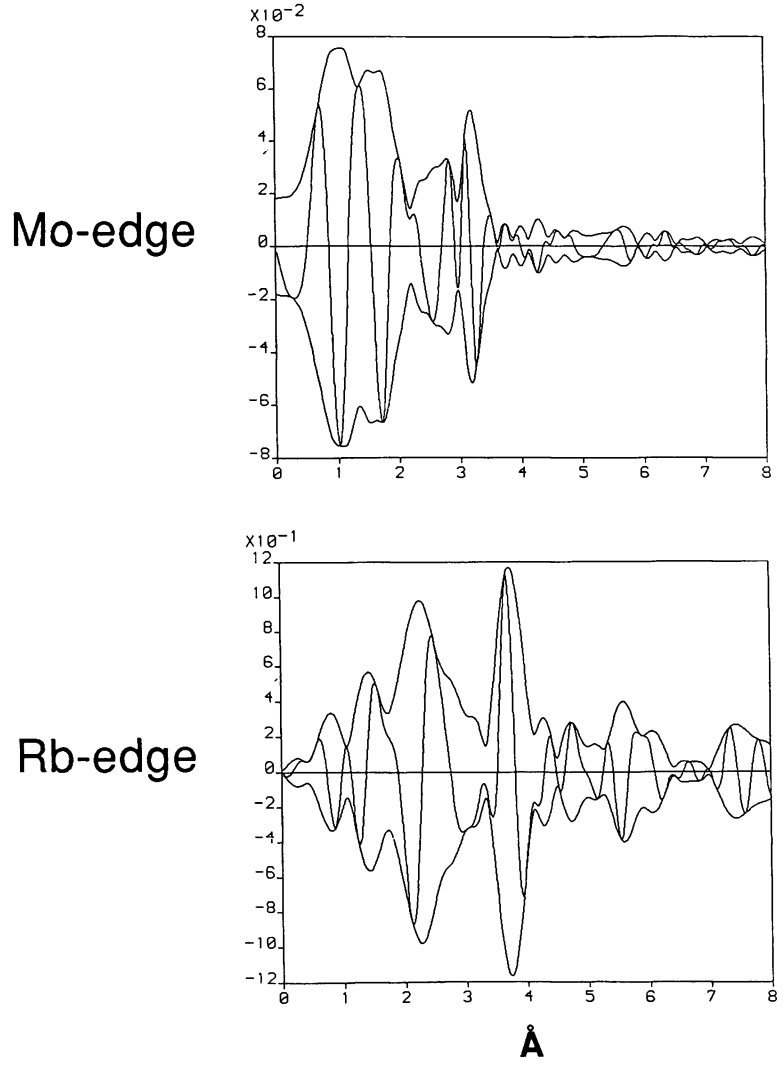

Figure 6: EXAFS data: top: Mo-edge Fourier transformation of the composite TEOS + $H_3PMo_{12}O_{40}$ after Rb ion exchange. Bottom: Rb-edge: corresponding Fourier transformation of the above composite

This study shows that Keggin ions can be occluded in glassy substrates with no side products, by either assembling the components in the pores of pre-formed glass, or by in-situ formation in precursor gels. In porous glasses, ion exchange similar to bulk reactions is observed, and cations are shown to be coordinated to the metalate framework. These glass composite offer a potential for the design of thin films with ion exchange capability.

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