Monitoring the Growth of Polyoxomolybdate Nanoparticles in Suspension by Flow Field-Flow Fractionation

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Reduction reactions of molybdate in acidic, aqueous solution lead to colored, mixed-valent Mo\textsuperscript{V/VI} polyoxomolybdate (POM) species.\textsuperscript{1–5} The two-century-old mystery of the “molybdenum blues”\textsuperscript{6} exemplifies the difficulty in characterizing suspensions of POM particles. Müller, Liu, and co-workers revealed the fundamental compositions of the related “molybdenum browns”, including \( I_P \) symmetrical keplerates. In general, reduced molybdates assemble into nanometric species (Figure 1a). Light-scattering, small-angle X-ray scattering (SAXS), and microscopy show slow aggregation of \( \text{Na}_3\{\text{Mo}^{\text{VI}}\text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{Mo}^{\text{II}}\text{Mo}^{\text{I}}\} \cdot 400 \text{H}_2\text{O} \) and \( [\{\text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}}\text{Mo}^{\text{V}}\text{Mo}^{\text{I}}\text{Mo}^{\text{I}}\text{Mo}^{\text{I}}\} \cdot \text{ca.} \cdot 150 \text{H}_2\text{O}] \). Formation of POM nanostructures in the presence of polymers and surfactants has also been reported.\textsuperscript{10,14,17} Co-workers were able to use scattering methods to study aggregation of a suspension, although Liu and co-workers were able to use scattering methods to study aggregation in lighter colored\textsuperscript{10,14,17} species (Figure 1a).

The \( \{\text{Mo}_{132}\} \) system is well suited for this investigation. Partial reduction of \( (\text{NH}_4)_6\text{Mo}_{124}\text{O}_{372}\text{H}_{72}\text{Fe}_{30}\text{H}_2\text{O} \) with \( \text{NH}_2\text{H}_2\text{SO}_4 \) in \( \text{CH}_3\text{CO}_2\text{NH}_4 \cdot \text{CH}_3\text{CO}_2\text{H} \) buffer produces crystals of \( (\text{NH}_4)_2\{\text{Mo}^{\text{VII}}\text{Mo}^{\text{VI}}\text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{Mo}^{\text{III}}\} \cdot \text{ca.} \cdot 300\text{H}_2\text{O} \). The \( \{\text{Mo}_{132}\} \) keplerate anion is \( I_P \) symmetrical with charge \(-42 \) and diameter ca. 2.9 nm.\textsuperscript{3,5,16} Light-scattering methods are hindered by the deep color of the \( \{\text{Mo}_{132}\} \) suspension, although Liu and co-workers were able to use scattering methods to study aggregation in lighter colored\textsuperscript{10,14,17} \( \{\text{Mo}_{154}\} \) and \( \text{Mo}_2\text{O}_3/\text{triblock copolymers} \).\textsuperscript{12,13} Although Müller and co-workers have studied surfactant-encapsulated \( \{\text{Mo}_{132}\} \)\textsuperscript{11} and oxidized \( \{\text{Mo}_{132}\} \) species\textsuperscript{8,9} and Cammers et al. have kinetically coprecipitated \( \{\text{Mo}_{132}\} \), with tripodal hexammincrown ethers,\textsuperscript{20} the evolution of nanometer species of an unperturbed \( \{\text{Mo}_{132}\} \)-derived suspension is uninvestigated.

The key methodology of our study is field-flow fractionation (FFF), a flow-based, chromatography-like separation and sizing technique that can monitor changes in the particle-size distribution of a suspension in situ. FFF is conducted in a thin, empty channel, \textsuperscript{21–23} which is well suited for this investigation. Partial reduction of \( (\text{NH}_4)_6\text{Mo}_{124}\text{O}_{372}\text{H}_{72}\text{Fe}_{30}\text{H}_2\text{O} \) with \( \text{NH}_2\text{H}_2\text{SO}_4 \) in \( \text{CH}_3\text{CO}_2\text{NH}_4 \cdot \text{CH}_3\text{CO}_2\text{H} \) buffer produces crystals of \( (\text{NH}_4)_2\{\text{Mo}^{\text{VII}}\text{Mo}^{\text{VI}}\text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{Mo}^{\text{III}}\} \cdot \text{ca.} \cdot 300\text{H}_2\text{O} \). The \( \{\text{Mo}_{132}\} \) keplerate anion is \( I_P \) symmetrical with charge \(-42 \) and diameter ca. 2.9 nm.\textsuperscript{3,5,16} Light-scattering methods are hindered by the deep color of the \( \{\text{Mo}_{132}\} \) suspension, although Liu and co-workers were able to use scattering methods to study aggregation in lighter colored\textsuperscript{10,14,17} \( \{\text{Mo}_{154}\} \) and \( \text{Mo}_2\text{O}_3/\text{triblock copolymers} \).\textsuperscript{12,13} Although Müller and co-workers have studied surfactant-encapsulated \( \{\text{Mo}_{132}\} \)\textsuperscript{11} and oxidized \( \{\text{Mo}_{132}\} \) species\textsuperscript{8,9} and Cammers et al. have kinetically coprecipitated \( \{\text{Mo}_{132}\} \), with tripodal hexammincrown ethers,\textsuperscript{20} the evolution of nanometer species of an unperturbed \( \{\text{Mo}_{132}\} \)-derived suspension is uninvestigated.

The key methodology of our study is field-flow fractionation (FFF), a flow-based, chromatography-like separation and sizing technique that can monitor changes in the particle-size distribution of a suspension in situ. FFF is conducted in a thin, empty channel, \textsuperscript{21–23} with separation based on relative hydrodynamic behavior.\textsuperscript{21–23} In flow field-flow fractionation (FIFFF), a cross-flow perpendicular to the direction of laminar channel flow forces dissimilar particles to different levels in the channel, where they are eluted at different flow velocities. FIIFF fractograms monitoring the absorbance of the eluate at 455 nm are shown in Figure 1b.

The particle-size distributions calculated\textsuperscript{26} from the data in Figure 1b have diameters ranging from 3 to 75 nm, roughly distributed in three populations with maxima about 3.4, 12, and 25 nm. The mean diameter is 31(±1) nm (confidence level 95%), averaged over 24 FIIFF runs from 8 days. The baseline fractogram at 10 min indicates that no particles over ca. 3 nm had yet formed. At 2 h, the 3.4-nm population is largest. The total area under the fractogram increases rapidly from 2 to 8 h, at which time the 12- and 25-nm populations are larger. We suggest that the 3.4-nm particles, decreasing after 2 h but observed consistently throughout the entire period, are the \( \{\text{Mo}_{132}\} \) with their associated counterions and solvation shell. The overall particle population reaches a maximum at ca. 8 h, decreases rapidly for about 2 days and more slowly thereafter (Figure 1b). The decrease parallels the precipitation of large particles that are not sampled by FIFFF shown in the SEM\textsuperscript{27} image in Figure 2a. The precipitate is in dynamic equilibrium with species still in solution or suspension, yielding after several days ca. 0.1-mm octahedral crystals of \( \{\text{Mo}_{132}\} \), \( Fm\overline{3} \) with \( a \approx 46 \, \text{Å} \),\textsuperscript{15} shown in Figure 2b.

The particle-size distribution of the molybdate suspension was corroborated by AFM, SEM, and HRTEM. Good agreement between particle-size distributions obtained by FFF and microscopy suggests that the POM superstructures are stable to FIFFF channel- and cross-flows, isolation and storage in air, and vacuum treatment in the electron microscopes. In other experiments, we established that the size distribution is unchanged by dilution or the presence of Triton X-100 surfactant. AFM images\textsuperscript{28} display roughly spherical particles in the 20–35 nm size range and agglomerates of these particles. Figure 2c shows a typical HRTEM\textsuperscript{29} image of \( \{\text{Mo}_{132}\} \)-derived particles after 1 day. Measurement of about 400 particles on several HRTEM images gives a range from 4 to 80 nm diameter with mean 34(±2) nm (confidence level 95%). Figure 2c reveals the hollow nature of the POM nanostructures. Each particle consists of a darker ring surrounding a circle of nearly uniform intensity, especially in the presence of the relatively high concentration of Triton X-100. Absorption at 455 nm in the UV/visible spectra of collected FIIFF fractions suggests that the nanoparticles consist of \( \{\text{Mo}_{132}\} \) units or chemically similar species. Müller and Liu have suggested similar superstructures in suspensions of related \( \{\text{Mo}_{154}\} \)\textsuperscript{28} and \( \{\text{Mo}_2\text{Fe}_{30}\} \).\textsuperscript{10,14,17}

In a \( \{\text{Mo}_{132}\} \) suspension, molybdenum can end up in three different forms: (1) suspended particles larger than 3 nm, which are eluted through the FIFFF detector; (2) soluble species and suspended particles smaller than 3 nm, which are removed by the cross-flow\textsuperscript{25} and do not pass through the FIFFF detector; (3) precipitate, which is not sampled for FIFFF. Measuring the Mo content of FIIFF eluate fractions by ICP-OES\textsuperscript{30} provides an independent, quantitative assay of the molybdenum distribution. Figure 1c compares Mo content in the suspension estimated by...
summing the total area of FIFFF fractograms (expressed as “relative particle mass”), assuming that the mass concentration of particles in the eluate is proportional to the UV detector signal and the particles have a constant density) vs the ICP-OES of eluate. The Mo distribution across a fractogram taken on day 3 is shown in Figure 1c. Above 25 nm in diameter, the FIFFF and ICP-OES curves are closely parallel. Below 25 nm in diameter, there is a secondary peak at 12 nm, and the Mo content by ICP-OES is much higher than by FIFFF. The discrepancy vanishes if abundant molybdate particles smaller than 25 nm do not have the keplerate-like structure of the larger particles, absorbing less strongly at 455 nm. The UV/visible spectra of a set of FIFFF fractions after day 3 shows a different molybdate species.

Figure 1. (a) Partial reduction of [MoO$_4$]$^{2-}$ (b) Fractograms of {Mo$_{132}$} nanoparticle growth over 7 days. (c) Mo content from summed area of FIFFF fractograms (relative particle mass) vs ICP-OES of eluent ([Mo] in fraction) on day 3. (d) Mo content per unit particle volume on day 3.

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References
(25) FFFractionation LLC Universal Fractometer model F1000, carrier liquid Milli-Q water containing 0.007% (w/v) Triton X-100 and 0.02% (w/v) Na$_2$CO$_3$, channel flow 0.50 mL/min, cross-flow 3.00 mL/min, regenerable cellulose membrane with 10 000 amu (~2.2 nm) cutoff, detector at 455 nm, no light-scattering correction.
(26) Postnova analytics, version 2.0; FFF Analysis software.
(27) Hitachi S900 field-emission SEM.
(28) Digital Instruments NanoScope IIIa, glass substrate.
(29) JEOL 2010F field-emission TEM.
(30) Varian Vista-Pro CCD, Mo detection at 396.152 nm.