Glenn T. Seaborg Center Seminar

Technetium-99 complexes of polyoxometalates: understanding the chemistry of technetium-99 incorporated into metal oxide matrices.

Lynn C. Francesconi
Hunter College and
The Graduate School of the City University of New York

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4:00 - 5:00 pm
Building 70A, Room 3377

Technetium-99 (^{99}Tc) ($t_{1/2}$: 2.1 x 10^5 years; β_{max}: 293.7 keV), a redox active metal, is a major product of uranium and plutonium fission. Controlling the extensive redox chemistry is one of the obstacles in identifying and developing a robust, scientifically based wasteform for Tc. The challenges that need to be addressed are 1) to identify strategies that will facilitate selective and tunable separation of ^{99}Tc from current and future spent fuel, tank wastes, and any waste stream from future nuclear activities, and 2) regardless of the originating source, to identify and develop a wasteform for storage and immobilization of ^{99}Tc under a variety of potential repository conditions.

To address these challenges we need to garner fundamental knowledge of the chemistry, redox speciation, and stability of technetium-99 incorporated into host molecules and materials. To achieve this objective our research is aimed towards providing a molecular level understanding of the chemical and redox stability of ^{99}Tc adsorbed to and incorporated into molecular metal oxides called polyoxometalates (POMs). An example of one family is given in **Figure 1**. POMs, nanometer sized metal oxide materials that possess specific and distinct defect sites for incorporation of redox active metal ions, serve as "models" to identify coordination environments that will enhance stability of low valent ^{99}Tc. We found also that POMs, in their own right, serve as photocatalysts for the reduction of $^{99}TcO_4^-$ to low valent Tc.

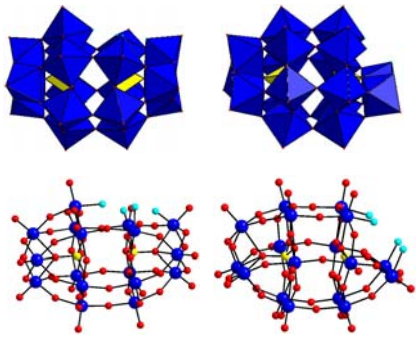

Figure 1. Polyoxometalates (POMs): ideal models for metal oxides. POMs are used to extract molecular level information on ^{99}Tc interactions with metal oxides. Top: polyhedral representation; Bottom: ball and stick representation. A: "lacunary" $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer ca. 1.2 nm in length and 0.6 nm width; B: the $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ isomer. The well defined defect structures (shown in cyan) possess distinct and different electronic and steric features that impact chemical and redox speciation of ^{99}Tc .

A case study of ^{99}Tc incorporated into the $\alpha1$ and $\alpha2$ isomers of $P_2W_{17}O_{61}^{10-}$ (**Figure 1**) leads to the conclusion that $^{99}Tc(IV)$ is stabilized in the $\alpha1$ defect site compared to the $\alpha2$ site under aqueous conditions. This conclusion can be rationalized by the composition of the $\alpha1$ and $\alpha2$ defect sites. Syntheses of the $^{99}Tc(V)O$ complexes of $[\alpha_1 / \alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ POMs and characterization employing mass spectrometry, multinuclear NMR, X-ray Absorption Spectroscopy will be discussed. Electrochemical studies will be presented. Evaluation of $^{99}Tc(V)O$ $[\alpha_1 / \alpha_2\text{-}P_2W_{17}O_{61}]^{7-}$ as organic soluble salts and comparison with Re analogs provides further insight into the redox chemistry and stabilities of the complexes.

In a related study, we realized that polyoxometalates have unique tunable, electron transfer abilities that facilitate electron transfer to $^{99}TcO_4^-$ for reduction to low valent states. We have used this property for photocatalytic reduction of $^{99}TcO_4^-$ by POMs ($\alpha_2\text{-}P_2W_{17}O_{61}^{10-}$ and "Keggin" POMs, namely, $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, $AlW_{12}O_{40}^{5-}$). The low valent ^{99}Tc is incorporated into the $\alpha_2\text{-}P_2W_{17}O_{61}^{10-}$ defect as confirmed by multinuclear NMR, electrochemistry, and UV-Visible spectroscopy. We are characterizing the low valent ^{99}Tc products of the Keggin POMs.

Host: Corwin Booth (510) 486-6079 CHBooth@lbl.gov Admin. Assistant: Catherine Mendez (510) 486-5587
Ernest Orlando Lawrence Berkeley National Laboratory
One Cyclotron Road | Berkeley, California 94720 | Tel: 510.486.4000