Strategies for the Photoreduction of Tc-99 Pertechnetate to Low Valent Tc by Keggin Polyoxometalates

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18th Annual City Tech Poster Session

ABSTRACT

Technetium-99 (^{99}Tc) is a hazardous radiological contaminant, which in its predominant form of pertechnetate (TcO_4^-) is highly mobile in the environment. Most strategies for the removal of pertechnetate from the environment involve uptake and or absorption of pertechnetate using resins, clays, and cationic metal-organic frameworks. In this work, we investigate using the "plenary" Keggin polyoxometalates (POMs), ($XW_{12}O_{40}^{n-}$)(X = P, Si, Al, n = 3, 4, 5) as a photocatalyst to both reduce TcO_4^- and stabilize the reduced Tc species. We report on the mechanism by which the reduction of Tc occurs and find that these POMs promote the reduction of TcO_4^- from Tc^{VII} to lower valent states. X-ray absorption spectroscopy was used to confirm Tc^{IV} and Tc^{V} species.

INTRODUCTION

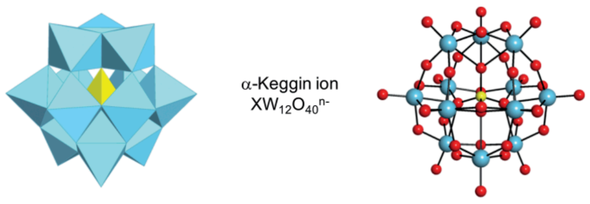

Figure 1.
The plenary $XW_{12}O_{40}^{n-}$ (X = P, Si, Al, n = 3, 4, 5), (XW_{12}) which can bind lower valent Tc on the surface. X yellow, W blue, O red.

^{99}Tc (half-life of $2.1x10^5$ years) is a high yield product of uranium-235 fission, which can be found in used nuclear fuel, nuclear waste, and the groundwater and soils near some nuclear facilities. Identification of disposal strategies for ^{99}Tc are central to many nuclear energy problems facing the US. Our approach employs a single material POMs, XW_{12} (Fig 1.) to reduce and sequester ^{99}Tc. POMs can be reversibly reduced using photocatalytic reduction in the presence of a sacrificial organic electron donor (SED).

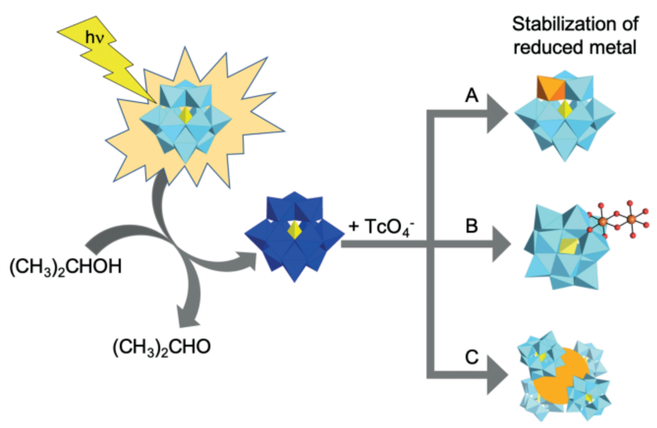

Figure 2.
The general strategy for photocatalytic reduction process of TcO_4^- by XW_{12}

1) XW_{12} is promoted to an excited state by irradiation.
2) The excited POM is reduced by a SED, 2-propanol.
3) The "reduced" POM transfers electrons to TcO_4^- which is reduced to low-valent ^{99}Tc.
4) Stabilization by the re-oxidized POM via: A) incorporation into a vacancy; B) binding to the surface of the POM; C) surface stabilization of Tc(0) by multiple POMs.

EXPERIMENTAL

XW_{12} was dissolved in 2 mL of 0.5 M H_2SO_4, D_2O, IPA (2:1:1 v.) at pH =1.13, and TcO_4^- was added. The sample was deoxygenated, stirred and irradiated:
1) exposed to sunlight (2 weeks), or 2) broad spectrum xenon lamp to mimic sunlight; 3) UV lamp (254 nm, 16h).

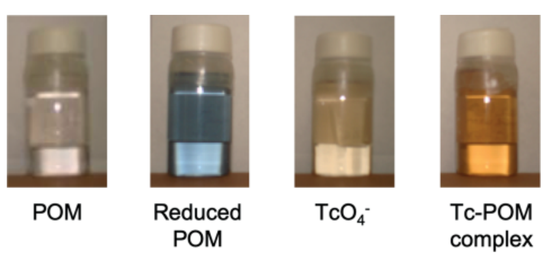

Figure 3.
Photocatalytic reaction with PW_{12} and TcO_4^-. The oxidized POM and TcO_4^- are colorless. The reduced POM is blue in color. Addition of TcO_4^- results in a red-brown Tc^{IV} complex.

RESULTS AND DISCUSSION

Sunlight photoreduction

POM/TcO_4^- ratio	Tc^{VII}	Tc^{V}	Tc^{IV}	Total reduced Tc[a]
PW_{12}; 10:1	0.17 (7)	0.1 (2)	0.7 (1)	0.8
SiW_{12}; 10:1	0.43 (5)	0.0 (1)	0.56 (8)	0.56
AlW_{12}; 10:1	0.72 (4)	0.0 (1)	0.28 (5)	0.28
PW_{12}; 20:1	0.07 (8)	0.2 (2)	0.7 (1)	0.9
SiW_{12}; 20:1	0.35 (6)	0.0 (1)	0.6 (1)	0.6
AlW_{12}; 20:1	0.63 (4)	0.0 (1)	0.37 (5)	0.37

[a] Reduced Tc represents the summation of Tc^{V} and Tc^{IV}.

Table 1. X-ray Absorption Near Edge Structure,(XANES) Spectroscopy data: The most effective reductant is PW_{12} > SiW_{12} > AlW_{12}. Some amounts of TcO_4^- remaining in solution.

Mechanism of TcO_4^- reduction

$$POM^{n-} + h\nu \rightarrow POM^{*n-} \quad (1)$$

$$POM^{*n-} + HO^iPr \rightarrow POM^{(n+1)-} + HO^iPr^{+\bullet} \quad (2)$$

$$POM^{(n+1)-} + TcO_4^- \rightarrow POM^{n-} + TcO_4^{2-} \quad (3)$$

$$2\ TcO_4^{2-} \rightarrow TcO_4^- + Tc^{V} \quad (4)$$

$$2\ Tc^{V} \rightarrow TcO_4^{2-} + Tc^{IV} \quad (5)$$

the rate-limiting step

The charge dictated by the central heteroatom allows tuning of the reduction potentials to match the potentials of Tc(IV) .

Xenon lamp broad spectrum irradiation

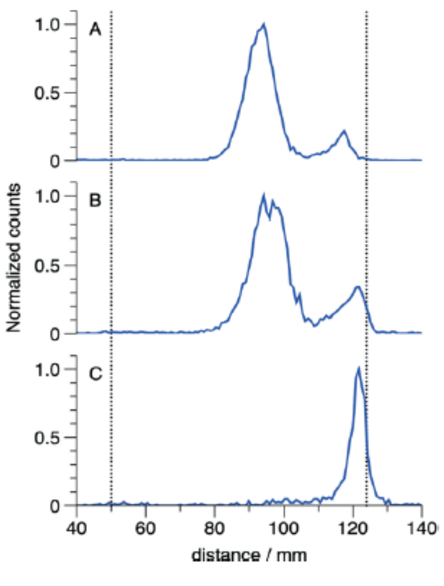

Figure 4.
Instant thin layer chromatography (ITLC) data for PW_{12}/ TcO_4^- at ratios of (A) 1:1, (B) 5:1, and (C) 10:1. Data shows increasing amount of reduced species (Rf = 0.9) with the increased amount of POM.

UV Irradiation

Sample	TcO_4^-	$Tc^{IV}\mu O_2$	$TcO_2 \bullet 2H_2O$
PW_{12}	0.06 (2)	0.72 (9)	0.22 (9)
SiW_{12}	0.07 (2)	0.76 (8)	0.18 (8)
AlW_{12}	0.12 (2)	0.73 (8)	0.15 (8)

Table 2. XANES data: XW_{12} reduce majority of TcO_4^- to Tc^{IV}. Tc^{IV} μ-oxo dimers are the most prevalent species. UV light irradiates directly into the W=O molecular orbital to promote the POM into the excited state and produces a larger amount of reduced Tc^{IV} species compared to the broad spectrum lamp.

CONCLUSIONS

The aim of this work involved investigating the potential of "plenary" Keggin POMs to photocatalytically reduce TcO_4^- and stabilize reduced Tc species. POMs have sites that can stabilize different Tc oxidation states and can be useful to understand the coordination chemistry of reduced Tc. We demonstrated photreductions where POMs dictate the Tc^{IV} and some Tc^{V} .These results pave the way for the investigation of solid-state materials for photocatalytic reduction of TcO_4^-.

REFERENCES

Ivana Radivojevic Jovanovic*, Colleen M. B. Gallagher*, Ramsey Salcedo, Wayne W. Lukens, Jr, , Benjamin P. Burton-Pye, Donna McGregor, and Lynn C. Francesconi (*contributed equally), Eur. J. Inorg. Chem. **2020**, 2133–2142