

Reaction of Aqueous Polyoxometalates with Silver and Gold Surfaces

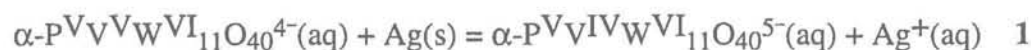
Jason Daniel Powell

Final Seminar

August 3, 2001

Oxide films play important roles in many fields including catalysis,¹ microelectronics,² and corrosion protection.³ Previous studies showed that α - $\text{SiW}_{12}\text{O}_{40}^{4-}$ (ST(4-)) anions self-assemble on Ag(111)^{4,5} and Au(111)⁶ to form monolayers with local ordering. The intent of this work is to use the reaction of a redox-active polyoxometalate (α - $\text{PVW}_{11}\text{O}_{40}^{4-}$ (PVT(4-))⁸, and its reduced form, α - $\text{PVW}_{11}\text{O}_{40}^{5-}$ (PVT(5-))⁹ with the substrate (Ag(111) or Au(111)) to control the structure, composition, and reactivity of the oxide surface phase on metal surfaces.

Reaction of dilute aqueous sulfuric acid solutions of PVT(4-) with Ag(111) yields a new surface phase, hex-PVT/Ag. Scanning tunneling microscopy (STM) studies reveal that hex-PVT/Ag consists of large, ordered domains with a hexagonal unit cell of edge length 1.34 ± 0.06 nm. In addition, the hex-PVT/Ag structure is always formed on Ag(111) immersed in acidic aqueous PVT(4-) solutions. Studies utilizing UV-visible spectroscopy and inductively coupled plasma spectroscopy, coupled with silver-ion selective electrode measurements confirmed that the reaction of PVT(4-) with Ag proceeds according to Equation 1 to yield PVT(5-) and Ag^+ .



Comparing the reduction potentials for the two half reactions yields a +0.02 V potential for 1.^{10,11} This reaction also occurs in solutions containing mixtures of PVT(4-) and PVT(5-), but a large excess of PVT(4-) is required for the formation of hex-PVT/Ag. The hex-PVT/Ag surface phase remains on the Ag surface even after thorough rinsing, and the constituent polyoxometalate species was confirmed to have the same mole ratio as PVT molecules (1 P:1 V:11 W).

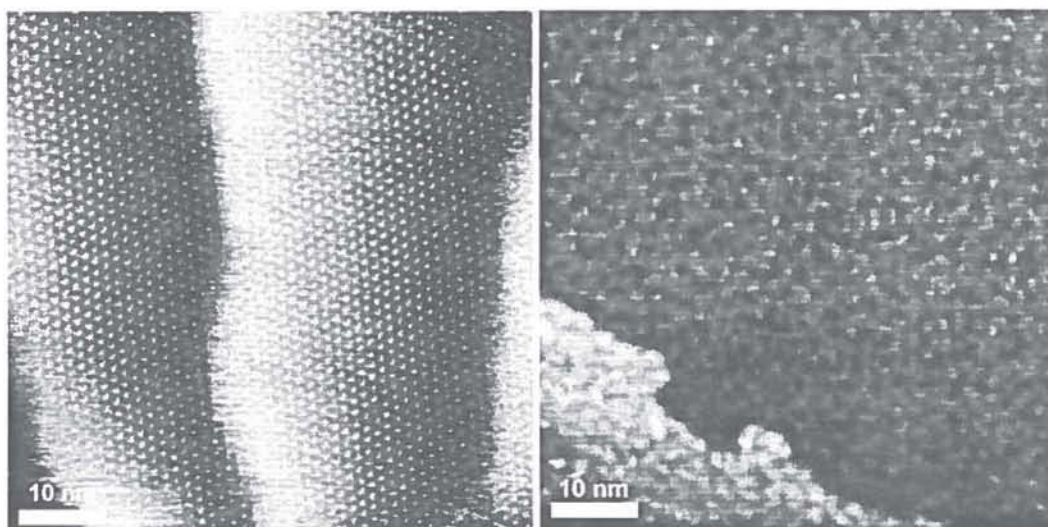


Figure 1

The reaction of Ag surfaces with acidic aqueous PVT(5-) solutions yields another new surface phase, a-PVT/Ag. This second surface phase is amorphous, and displays the electrochemical behavior of adsorbed PVT(5-). STM images comparing the structure of hex-PVT/Ag (left) with a-PVT/Ag (right) are shown in Figure 1.

Acidic aqueous solutions of both PVT(4-) and PVT(5-) react with Au(111) surfaces to form surface phases with limited translational order and possessing multiple domains. The PVT(4-) molecule forms a surface phase with small domains of multiple structures identical to those previously reported for ST(4-) on Au(111).⁶ In contrast, PVT(5-) forms smaller domains of only a single structure. Furthermore, domain sizes appear to be limited to a critical length. Molecules adsorbed around the periphery of the small domains are removed during the course of imaging by STM, but the nucleation sites associated with each domain are not as easily removed. Shown in Figure 2 are two STM images comparing the surface phases formed by PVT(4-) (left) and PVT(5-) (right) on Au.

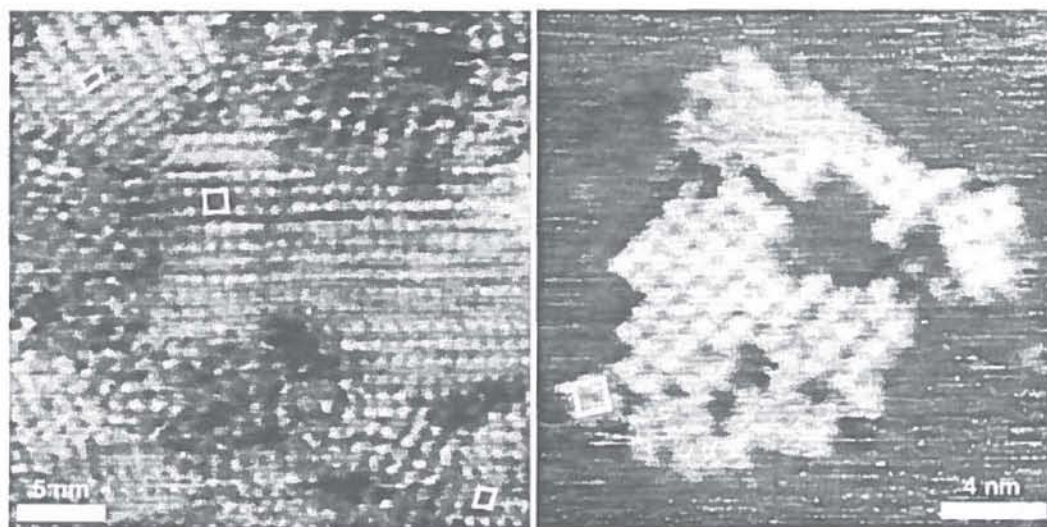


Figure 2

By using PVT(4-) and PVT(5-) as reagents, the structure, composition and reactivity of surface phases formed on Ag(111) and Au(111) were controlled. Of particular interest are the strongly bound surface phases hex-PVT/Ag and a-PVT/Ag, which are formed from PVT(4-) and PVT(5-) solutions, respectively. In contrast, PVT(5-) reacts with Au(111) to yield locally ordered domains that adhere more weakly to the surface.

References

1. Anderson, J. R.; Boudart, M. *Catalysis: Science and Technology*; Springer-Verlag: Berlin, 1981.

2. Elshabini-Riad, A; Barlow, F. D., III *Thin Film Technology Handbook*; McGraw-Hill: New York, 1997.
3. Talbot, D.; Talbot, J. *Corrosion Science and Technology*; CRC Press: Boca Raton, 1998.
4. Ge, M.; Zhong, B.; Klemperer, W. G.; Gewirth, A. A. Self-Assembly of Silicotungstate Anions on Silver Surfaces. *J. Am. Chem. Soc.* **1996**, *118*, 5812-5813.
5. Ge, M.; Gewirth, A. A.; Klemperer, W. G.; Wall, C. G. A Structural Model for Silicotungstate (α - $\text{SiW}_{12}\text{O}_{40}^{4-}$) Monolayers on Silver (111). *Pure Appl. Chem.* **1997**, *69*, 2175-2178.
6. Ge, M.; Niece, B. K.; Wall, C. G.; Klemperer, W. G.; Gewirth, A. A. Structure of Monolayers of Silicotungstate Anions on Ag(111) and Au(111) Electrode Surfaces. *Mat. Res. Soc. Symp. Proc.* **1997**, *451*, 99-108.
7. Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.
8. Domaille, P. J. Vanadium(V) Substituted Dodecatungstophosphates. *Inorg. Synth.* **1990**, *27*, 96-104.
9. Smith, D. P.; So, H.; Bender, J.; Pope, M. T. Optical and Electron Spin Resonance Spectra of the 11-Tungstovanado(IV)phosphate Anion. A Heteropoly Blue Analog. *Inorg. Chem.* **1973**, *12*, 685-688.
10. Smith, D. P.; Pope, M. T. Heteropoly 12-Metallophosphates Containing Tungsten and Vanadium. Preparation, Voltammetry, and Properties of Mono-, Di-, Tetra-, and Hexavanado Complexes. *Inorg. Chem.* **1973**, *12*, 331-336.
11. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; John Wiley & Sons: New York, 2001.