**The Preparation and Chemical Reaction Kinetics of
Tungsten Bronze Thin Films and Nitrobenzene with and without a Catalyst**

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ABSTRACT

Microcrystalline tungsten bronze thin films were prepared using wet chemical techniques to reduce a tungsten oxide thin film that was prepared by thermal oxidation of a sputter deposited tungsten metal film on a quartz substrate. The crystallinity of these films was determined by X-ray diffraction and the surface was characterized by X-Ray and Ultra-Violet Photoelectron spectroscopy. The total amount of hydrogen incorporated in the film was monitored using absorbance spectroscopy at 900 nm. The oxidation kinetics of the film and the hydrogenation of nitrobenzene in hexane were measured as a function of film thickness. A satisfactory fit of the resulting kinetics was obtained using a model that involves two simultaneous processes. The first one is the proton diffusion from the bulk of the film to the surface, and the second is a reaction of the surface protons with the oxidants. Finally, the dependence of the reaction rates on the presence of catalytic amounts of first row transition metals on the surface of the film was explored.

KEYWORD: Tungsten Oxide, Tungsten Bronze, Hydrogenation, Macroscopic Kinetics, UV-Vis

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INTRODUCTION

The hydrogen bronzes of molybdenum and tungsten are interesting compounds derived from the reduction of molybdenum or tungsten trioxide with hydrogen or a hydrogen source such as an alcohol.[1-6] These mixed valence oxide species are highly-colored compounds that contain pentavalent metal centers attached to hydroxides. The attached hydroxides have the unusual property of reacting as if they are hydridic rather than in the expected protic manner.[2] This reaction behavior is due to the fact that the transfer of the hydrogen ion is accompanied by electron transfer and reoxidation of the metal ion back to the hexavalent state. In some respects, the bronze can be considered to be a convenient storage medium for reactive hydrogen and this property has been exploited in hydrodechlorination of chlorocarbons.[1; 7] A later investigation found that these reagents neutralize both peroxide-based improvised explosives and military explosives (such as RDX and TNT) under ambient conditions during which a dramatic color change is observed.[8] For the military explosives, the process is suspected to occur via a reduction of the nitro groups to amines. To investigate the surface chemistry occurring during the reduction of the nitro-based explosives and oxidation of the bronze, this paper discusses the development of a model system, based on tungsten oxide films that mimic these nanometric materials.

Films of tungsten oxide exhibit a wide spectrum of electrochromic and photochromic properties.[9-13] Chromogenic properties of evaporated tungsten oxide films were first intensively explored by S. K Deb in 1970s.[14] The observed alteration of its optical properties in response to the external stimuli (light, temperature, and applied voltage) makes tungsten oxide one of the most promising chromogenic materials for a wide range of applications.[15] The ability to reversibly change color creates opportunities for its use in emerging technologies, especially for highly energy efficient buildings with incorporated “smart windows.” [16] Other possible applications for optical switching films include sensors for noxious gases, [17] hydrogen sensors, [18] adjustable surface emissivity devices for satellite applications,[19] UV and Co-60 radiation detectors, electrochromic displays, and variable reflectance mirrors.[20]

The mechanism of WO₃ hydrogenation (reduction) follows the scheme:

The reverse reaction occurs upon reaction with an oxidizing agent. Given that chemical reactions occur at the surface, a relevant parameter is the diffusion coefficient for hydrogen to migrate from the bulk of the sample towards the surface. A diffusion constant (D) can be written that includes both diffusion of the H⁺ ion and the electron. It is shown that diffusion coefficient varies both with hydrogen content[21; 22] and deposition parameters as well as the density of the films.[23] The diffusion coefficient turns out to depend on the crystallinity and the hydrogen concentration of the bronze. In different electrochemical experiments, the reported values lie in the range of 1.5×10^{-9} to 3×10^{-12} cm²/s for approximately 500-nm-thick WO₃ films deposited by evaporation.[13; 23] The diffusion coefficient for hydrogen atoms in crystalline films is estimated to be several orders of magnitude greater than that in amorphous WO₃ films.[24] Indeed, NMR kinetic studies resulted in an extrapolated value for D of 7×10^{-6} cm²/s at room temperature.[25] The rate of hydrogen insertion is also related to the presence of water in the reaction (reduction) media. Bludska *et al.* reported that water increases the rate of hydrogenation and that the rate also becomes greater with an increase in the number of reduction-oxidation cycles.[26]

EXPERIMENTAL

Three different preparative methods were explored: sputter deposition followed by oxidation, evaporative deposition and sol-gel deposition. As discussed later, the sputter deposition oxidation method was chosen for all the kinetic studies in this paper. For this method, quartz slides measuring 0.5 cm x 2 cm were pretreated by heating in a solution of 1:3 ratio of 30% (v/v) hydrogen peroxide and 18.0 M sulfuric acid. This process removes any organic matter and hydroxylates the surface. We found that organic residues result in poor adhesion of the initially sputtered metal coating. The ion beam sputtering was performed in a vacuum chamber under a vacuum of 1×10^{-6} Torr. Pure argon gas for 2.5 cm × 22 cm linear ion source and a plasma bridge neutralizer were controlled by a GFC-1000-U gas flow controller (Ion Tech, INC.) at 4.0 sccm and 2.0 sccm, respectively. The energy for the argon ion beam voltage was 900 V during

deposition, controlled by MPS-3000 power supply (Ion Tech, INC.). A Maxtek thickness monitor (TM-350/400) was used with a crystal-based microbalance to measure the rate of deposition. The sputtering rate of the described apparatus was measured to be $2.0 \text{ \AA/sec}$. The substrates were rotated at 10 rpm during the deposition and were positioned 20 cm from a tungsten metal target. The resulting tungsten metal films were then annealed in a Thermolyne 21100 tube furnace under an oxygen atmosphere at 600°C for 4 hours to create tungsten oxide films. X-ray diffraction (XRD) patterns recorded using a Bruker Advance D8 diffractometer (copper K_α radiation) of these films showed only one broad peak, implying an amorphous film. The samples were oxidized within a quartz tube by a stream of gaseous oxygen at one atmosphere and heating up to 450°C for three hours to produce slightly yellow WO_3 films on the quartz substrate. The oxidation step was the main reason for the use of a quartz substrate as opposed to cheaper borosilicate glass slides due to the tendency of the tungsten oxides to pull impurities out of the glass slides during oxidation. The final thickness of the oxide film was calculated using the thickness reported by the crystal-based microbalance corrected for the rotation of the sample during disposition and the density difference between the W metal and its oxide. The assumption is that the film's surface length and width was constant and the only change upon oxidation was in the thickness.

The colored H_xWO_3 films were created via the reaction of tungsten oxide films with nascent hydrogen released using zinc metal and hydrochloric acid. As a result, colored tungsten bronze are produced. For most preparations, the slide was placed in a container with 5 mL of 1 M hydrochloric acid. Approximately 1 gram of powdered zinc metal was added and the inhomogeneous mixture was swirled by hand until the reaction between the acid and the zinc was complete. The samples formed using the wet chemistry method were compared to tungsten oxide films reduced by atomic hydrogen generated by splitting molecular hydrogen on a hot filament in an UHV-chamber for 3.5 hours. During deposition, the temperature of the sample was recorded to be 369 K and pressure of hydrogen in the chamber was equal to 1×10^{-5} Torr. Both methods resulted in the formation of stable blue H_xWO_3 films.

In addition to films made using sputtering followed by oxidation, films were also created using either direct thermal evaporation of the oxide or sol-gel chemistry. For thermal evaporation, tungsten (VI) oxide (99.8%, Alfa Aesar) was deposited directly onto cleaned (as described above) 3" x 1" x 1 mm microscopic slides (Fisher Scientific) by performing repetitive conventional thermal evaporation technique under a vacuum of 1×10^{-5} Torr. For direct thermal evaporation of the oxide, an electrically heated tungsten-coated foil boat (MDC) was fixed 10 cm directly below the substrate. The manually manipulated deposition rate is a function of applied voltage and ranges from 10.0 to 30.0 Å/sec. For the sol-gel approach, a colloidal tungsten oxide films was produced using tungstic acid generated from sodium tungstate by an ion-exchange column. A solution of 1.0 M sodium tungstate dihydrate (99%, Sigma-Aldrich) was eluted through a column containing analytical grade cation exchange resin AG 50W-X2, 50 – 100 mesh in its hydrogen form (Bio-Rad). This produces a tungstic acid solution that was deposited onto cleaned 3" x 1" x 1 mm microscope slides (Fisher Scientific). The sol-gel films were dried at room temperature for 24 hours and were usable for a few days. The bronze films were prepared with hydrogen released by the oxidation of zinc metal with hydrochloric acid as described above.

The XPS and UPS equipment used in this investigation has been previously described.[27] Briefly, it consists of a surface analysis system with a typical base pressure of 2×10^{-10} Torr measured using an uncorrected nude ionization gauge. The XPS measurements were performed using the Mg anode of a PHI 300 Watt Twin Anode X-ray source. The resulting photoelectrons were detected by a PHI double-pass cylindrical mirror analyzer (CMA) with a pass energy of 50 eV. UPS was implemented using a differentially pumped He discharge ultra-violet source (UG Microtech) to provide He(I) radiation. The same double-pass cylindrical mirror analyzer with a pass energy of 5 eV was used to detect the resulting photoelectrons. A copper foil provides the Fermi level reference for the UPS photoelectron energies. XRD measurements were performed using a Bruker D8 Advance X-ray powder diffractometer with indexing, crystallite size, search/match, and quantitative analysis capabilities. Finally, UV-Vis spectra were recorded manually using a DMS-200 Dual-Beam Spectrophotometer with a beam size of

2 x 8 mm.

Control experiments showed that impurities in the hexane slowly reacted with the bronze films. Therefore the hexane was purified by shaking with concentrated sulfuric acid followed by vacuum distillation under nitrogen from sodium benzophenone ketyl solubilized with tetraglyme. Once purified, the H_xWO_3 films were indefinitely stable immersed in the hexane. It was also found that continuous exposure to the 900 nm light from the spectrometer source also impacted the rate measurement. For this reason, the hydrogen bronze, the samples were stored in the dark after their preparation and were exposed to the 900 nm radiation only for the time needed to obtain an absorbance measurement (less than 1 min).

RESULTS AND DISCUSSION

Film Preparation

The synthetic method used for the preparation of tungsten oxide films can strongly influence their properties. For example, thin films produced using one method can have an electrochromic sensitivity extremely different from that of films produced by other methods.[28] Surface defects, oxygen vacancies and interstitials may be responsible for optically active materials obtained under different deposition conditions.[29] In addition, absorbed water can increase the surface conductivity and thus enhance the proton mobility required for efficient electrocoloration.[30] To understand how the properties are affected by different deposition methods, tungsten oxide films were produced by sputter deposition followed by oxidation, evaporative deposition and sol-gel deposition. Films of tungsten oxide formed using sol-gel or thermal evaporation were found to be significantly less reactive in comparison to films prepared by sputter deposition followed by oxidation. Although the colloidal films had excellent electrochromic properties, the surface had the least reactivity compared to the other preparation methods, possibly due to a greater amount of impurities incorporated during film preparation and drying. The thermal evaporation of tungsten oxide produced a light blue film, possibly due to oxygen defects that resulted in less hydrogen incorporation. This film also had lower surface reactivity and the color change during the formation of the bronze was less intense.

Interestingly, both the films prepared by sol-gel and by the thermal evaporation of tungsten oxide performed better in electrochromic applications. Possibly, materials produced by these methods have better electrical conductivity due to bulk defects that are removed from the oxide film during the annealing process.

Given that the focus of this research was chemical reactivity of the surface toward nitro containing organic compounds, the films formed by sputter deposition followed by oxidation method for tungsten oxide films were selected for the studies presented in this paper. This method produced transparent thin films of tungsten oxide. XPS showed little surface contamination and little absorbance in the UV-VIS spectrum between 600 and 1000 nm, implying minimal oxygen defects. In contrast, the thermal deposition of tungsten oxide from an oxide source resulted in colored films. A 210 nm thick WO_3 film was utilized for the studies below. Unless noted in the text, the bronze film was created via the reaction of tungsten oxide films with nascent hydrogen released by the reaction of zinc metal with hydrochloric acid.

Film Characterization

The thermal oxidation of the tungsten films result in a polycrystalline cubic phase (Figure 1A), that was previously observed for tungsten oxides after annealing to higher temperatures.[31] The lattice parameter was determined to be 3.7507 Å. Figure 1B shows the corresponding H_xWO_3 XRD spectrum. It is also cubic with a lattice parameter equal to 3.700 Å. This lattice constant implies a tungsten bronze with a hydrogen content of $x \geq 0.5$. Analogous results were obtained for the bronzes prepared by refluxing WO_3 with iso-butanol for 12 hours.[32]

Figures 1. (A) XRD for a typical WO_3 film and (B) H_xWO_3 film. Both films were deposited on a quartz substrate. The data implies a cubic phase with a lattice parameter of $3.700 \text{ \AA}$. For the H_xWO_3 film, this parameter is consistent with a hydrogen content of $x \geq 0.5$.

The XPS spectrum of a typical H_xWO_3 film is shown in Figure 2A. This film was reduced ex-situ using zinc and hydrochloric acid. The spectrum is identical to a H_xWO_3 film generated in the UHV-chamber using atomic H (see experimental), with the exception that this process removed surface contaminants adsorbed during the transfer into the UHV chamber. Three peaks attributed to W are clearly seen: a doublet W $4d$ at 261.3 eV and 246.4 eV and a broad peak at 35 eV corresponding to the splitting between $4f_{7/2}$ and $4f_{5/2}$ levels. A strong peak at 530.5 eV attributed to O $1s$ is also observed. The two peaks at 743 eV and 764 eV can be identified as the oxygen KLL Auger peaks that are consistent with the results reported by Barreca et al.[33] The spectra of H_xWO_3 thin films are practically indistinguishable from nanometric H_xWO_3 synthesized using the method by Apblett *et al* (Figure 2B).[8]

Figure 2. XPS spectra of a (A) H_xWO_3 thin film deposited on quartz and generated ex-situ using zinc and hydrochloric acid and (B) H_xWO_3 nanometric material.

The deconvoluted W $4f$ peak for WO_3 is shown in Figure 3A. Gaussian-Lorentzian fitting was used for the analysis. Photoelectron binding energies were calibrated with respect to the C $1s$ peak centered at 284.6 eV. The W $4f$ peak consists of a doublet due to spin-orbit splitting between $4f_{7/2}$ and $4f_{5/2}$ levels. The separation of the peaks in the doublet is constant and equal to 2.15 eV. The doublet corresponds to a $4f_{7/2}$ line with a binding energy of 35.4 eV corresponding to the presence of W^{6+} species in the film.[33] The XPS O $1s$ spectrum (not shown) for a WO_3 film has a main component centered at 530.4 eV that is attributed to oxygen in a WO_3 film. There is another small peak at 532.4 eV due to the presence of water bound in the film structure as well as water molecules adsorbed on the film surface. [34]

Figure 3B shows a high-resolution scan of the W $4f$ peak for H_xWO_3 . Three doublet components are observed. These phenomena can be due to the presence of mixed tungsten valences in H_xWO_3 . The given results are consistent with the data obtained by Yao *et al.* for electrodeposited films.[35] The first doublet with $4f_{7/2}$ at 35.6 eV corresponds to the W^{6+} oxidation state analogous to that in WO_3 . The second (32.0 eV) and third (29.7 eV) ones are believed to be due to the presence of W^{5+} and W^{4+} states,

correspondingly. The relative amounts of tungsten W^{6+} , W^{5+} and W^{4+} the relative amounts of tungsten W^{6+} , W^{5+} and W^{4+} on the surface of the H_xWO_3 films are 17, 55 and 285%, respectively. For a sample reduced within the UHV-chamber using atomic H (see experimental), the relative amounts of tungsten W^{6+} , W^{5+} and W^{4+} are 14, 49 and 37%, respectively. Given the number of peaks (see Figure 3B), the binding energies and percentages should be used only as a guide and not as absolutes. The higher percentage of W^{4+} seen on the surface, which respect to the sample generated using wet chemistry, is likely due to the formation of the bronze using an H-atom source in high-vacuum conditions. The presence of W^{4+} has also been observed for sputtered films. In addition, the high resolution O 1s XPS spectrum (not shown) for H_xWO_3 film has a component attributed to the O atoms in surface –OH groups, that has greater intensity than the analogous peak for the non-hydrogenated WO_3 spectrum. This result is consistent with the formation of additional O-H bonds in the process of hydrogenation. The spectra of the tungsten bronze films are practically indistinguishable from the nanometric material synthesized by chemical methods.[8]

Figures 3. (A) W $4f_{7/2}$ and $4f_{5/2}$ XPS for a typical WO_3 film and (B) for an H_xWO_3 film generated ex-situ using zinc and hydrochloric acid. Both films have been deposited on a quartz substrate.

UPS studies have previously been performed on tetragonal WO_3 as well as for cubic tungsten bronzes.[36-40] Pure single crystal WO_3 is characterized by a broad peak

appearing at about 7.5 eV.[36] The position of the top of the valence band for amorphous tungsten oxide is 4.1 eV, whereas for a polycrystalline one it is 3.65 eV.[38] Reduction of WO_3 to bronze results in broadening of the valence band peak and appearance of the additional small peak near the Fermi level that is believed to be due to partial filling of the conduction band in the process of bronze formation.[36] Figure 4A shows the UPS spectra of non-hydrogenated and H_xWO_3 films. In contrast to the results for tetragonal WO_3 , the UPS spectrum for cubic tungsten oxide obtained by thermal oxidation of W does not contain any peaks in the region from the Fermi level to 14 eV. Nevertheless, after reduction to a bronze, a broad peak with a maximum at 10 eV appears. Similar to tetragonal tungsten oxide, this peak can be assigned to the presence of extra electrons in the valence band and shifting of the Fermi level to higher energies. The intensity of the peak for the bronze obtained by hydrogenation in the UHV chamber is much higher than that of the film obtained by the wet chemical method, indicating larger concentration of hydrogen than is possible with just the nascent hydrogen created by the reaction of zinc with hydrochloric acid.

UV-Vis spectra of the WO_3 and tungsten bronze films (Figure 4B) produced by chemical reduction consistently show the extra near-infrared band appearing at $\lambda=1000$ nm in the case of bronzes. This wavelength corresponds to a band energy of 1.2 eV and can be attributed to the presence of electrons in the lower conduction band. Similar results were obtained for tungsten bronzes prepared by other methods.[12; 41-45]

Figure 4: (A) UPS spectra of an H_xWO_3 film (Bronze) and a non-hydrogenated WO_3 film (Oxide), and (B) UV-Vis absorbance spectra of 30 nm H_xWO_3 film (Bronze) and WO_3 film (Oxide) on quartz.

UV-VIS Study of the Reduction of Nitrobenzene

Using the H_xWO_3 model films, the kinetics of oxidation of tungsten bronze films and the simultaneous reduction of the nitro group on the nitrobenzene was studied by measuring the absorbance of the thin film with a DMS-200 UV-Vis Spectrophotometer. In this experiment, nitrobenzene was utilized as a surrogate for nitro-based explosives. The total amount of hydrogen incorporated in the film is proportional to the absorbance at 900 nm. By monitoring the disappearance of the 900 nm absorption peak, the oxidation kinetics of the film and hydrogenation of nitrobenzene in hexane can be measured. The experimental setup is described in the supplemental information. During the control experiment, it was found that impurities in the hexane and continuous exposure to light from the spectrometer source affected the reaction rate. Thus, the hexane was purified as discussed in the experimental, and the sample was kept in the dark and exposed to the 900 nm radiation only for the time needed to obtain an absorbance measurement (less than 1 min).

The first kinetic experiments were performed using a 3.0 M solution of nitrobenzene in ultra-pure hexane. At this concentration, the reaction rate is independent of the nitrobenzene concentration because it is in sufficient excess that its concentration can be considered constant. Figure 5A shows a typical reaction rate with time, while Figure 5B shows the natural log of the absorbance versus time for three film thicknesses. Given the linearity of the natural log of absorbance versus time plot, the system follows first order kinetics. In addition, the variation of the rate with thickness, or hydrogen concentration, implies that the rate is limited by the concentration of hydrogen at the surface. Thus, experimentally, the adsorption of nitrobenzene and the deposition of the product does not affect the measured reaction rate at the given nitrobenzene concentration.

Figure 5: (A) Absorbance at 900 nm versus time and (B) a natural log plot of the absorbance versus time showing first order kinetics for H_xWO_3 thin films of different film thickness normalized. For clarity, the initial absorbance was normalized to one. The data shown are for the reduction of 3.0 M nitrobenzene in ultrapure hexane.

Based on these experimental observations, a model of proton concentration distribution may be developed using four assumptions: (1) the absorbance is proportional to the hydrogen concentration in the film, (2) the initial concentration profile through the film is constant (hydrogen is uniformly distributed) and the hydrogen cannot diffuse into the quartz substrate, (3) the concentration of the nitrobenzene on the surface is constant, and (4) the product has a significantly fast desorption rate and does not affect the observed kinetics. The full derivation of the model is given in the supplemental material. The key assumption of this model is that the hydrogen diffusion in the bulk follows Fick's Law. The boundary conditions are that hydrogen cannot diffuse into the quartz substrate and that the loss of hydrogen (hydrogen ion and electron) occurs only at the reaction surface. Finally, the reaction rate is proportional to the surface concentration of hydrogen and the concentration of nitrobenzene. This assumption implies that complex processes on the surface (electron and proton transfer, adsorption and desorption) can be described by a single rate constant. We speculated that the chemical reaction between the nitro and the surfaces is the rate-limiting step. A numerical computation of the hydrogen profile with time is shown in Figure 6 for an arbitrary diffusion rate and reaction rate constant. The measured absorbance values are related to the integration of the hydrogen concentration over the thickness of the film.

Figure 6. Time dependent proton concentration distribution in a tungsten bronze film with thickness L . At time equal zero, the concentration is constant. For longer times the concentration at the surface decreases and a concentration gradient forms into the bulk.

For the conditions described here, it is the concentration of hydrogen at the surface that determines the reaction rate. Thus, a relationship between the thickness and the inverse of the measured rate constant or relaxation time is

$$\tau = \frac{4}{\pi^2 D} L^2 + \frac{1}{k_f C_{ox}} L,$$

where, D is the hydrogen diffusion constant, L is the thickness of the film, k_f is a reaction flux, C_{ox} is the surface nitrobenzene concentration, which is assumed to be constant. The origin of this equation is discussed further in the supplemental material. A similar analysis was used by Kikuchi *et al.* to study the thickness dependence bronze films produced from vacuum deposited WO_3 and oxidized using $Fe_2(SO_4)_3$. [10] Figure 7 shows the relaxation time (τ) vs film thicknesses (L) between 250 – 2500 Å. Each point represents at least three kinetic experiments with a nitrobenzene concentration of 3.0 M.

Figure 7: Measured relaxation time versus film thickness. The relaxation time is the reciprocal of the first order reaction rate for the reduction of a 3.0M nitrobenzene solution in ultrapure hexane.

Using this data, the value of the diffusion coefficient, D , is estimated to be $10^{-13} \text{ cm}^2/\text{s}$, which is consistent with the values obtained in various electrochemical experiments, given the overall rate appears (due to its high degree of linearity with thickness) to be dominated by the surface reaction rate. Similar results were obtained from analogous data for the room temperature air oxidation of tungsten bronze thin films prepared by UV-illumination of WO_3 films.[46]

Catalysis Effects

It was observed experimentally that the addition of small concentrations of silver ions to the bronze nanometric materials was effective in changing the rate of hydrogen transfer. Kinetic experiments were performed on 105 nm thick films coated with different concentrations of silver using 3.0 M nitrobenzene in hexane as a probe molecule. Silver was deposited on WO_3 films by using the reducing power of H_xWO_3 , where silver replaces hydrogen of the bronze.

After preparation of the bronze films, they were submerged into a 0.1 M silver nitrate solution and allowed to reduce the silver ions. This process forms silver particles or islands on the WO_3 surface. The amount of silver is controlled by using films with different initial hydrogen concentrations quantified by the percent decrease in the absorbance of the films at 900 nm with respect to that of freshly prepared samples. This process involves first reducing the WO_3 films using zinc hydrochloric acid solution. Next, the films were allowed to oxidize in air until the absorbance at 900 nm is 0%, 15%, 25%, 50%, 75% and 100% of the respective initial absorbance. This partial oxidation allows films with different concentrations of hydrogen/ W^{5+} to be generated. After this, the films were submerged into the silver nitrate solution overnight. XPS measurements (see Supplemental Information) showed the deposition of silver on the surfaces. Silver is reduced by the oxidation of the bronze film to WO_3 . After forming the coated surface, the bronze must be regenerated using the zinc and hydrochloric acid method before the reaction rates are measured. Figure 8 shows the kinetic plots for the various coating.

Figure 8. Absorbance versus time for several Ag coated bronze films. The “No Ag” line is a bronze film before Ag deposition as a reference. The percent is the relative concentration of hydrogen within the film, with respect to the initial concentration, before coating with silver, and is proportional to the amount of

silver. The reaction rate of the surface with the highest amount of silver (100%) is slower than that of the bare bronze surface.

The fastest reduction rate for nitrobenzene was obtained using silver coated tungsten bronze films initially prepared from uncoated samples whose absorbance at 900 nm decayed to approximately 75% of the initial value. Exact quantification of the amount of silver on the surface is left to a future study. For higher concentrations of deposited silver, the reaction rate decreases as the bronze becomes buried under the silver film.

Using films whose absorbance at 900 nm decreased to approximately 75 % of the initial value, first row transition metals titanium (Ti), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni) and copper (Cu) were deposited on tungsten bronze film surfaces. In addition, palladium (Pd) was also deposited using on the bronze films. Pd was deposited because it is a good catalyst for hydrogenation reactions. The hope was that Pd would assist the transfer of hydrogen to the nitro group during the reduction. Additional information on the deposition procedure can be found in the supplemental information. The resulting rate constants for 3.0 M nitrobenzene on these coated bronze films are shown in Figure 9. The error bars are based on at least three independent measurements.

Figure 9. The effects of various metal coatings on the reaction rate for the tungsten bronze thin films with nitrobenzene.

In general, there appears to be a moderate increase in reaction rate increases with atomic number for the first row elements (Ti to Cu). Interestingly, the reaction rate of titanium-coated films is larger than expected based on the data for Cr, possibility due to a titanium hydroperoxide being used in the deposition instead of a metal salt. Some caution should be exercised in comparing the various catalysts, as the exact concentration of each element on the surface has not been determined.

Conclusions

Crystalline tungsten oxide thin films were prepared by sputter deposition of tungsten metal followed by subsequent oxidation. Hydrogenation was carried out by nascent atomic hydrogen released in the reaction of zinc metal with hydrochloric acid. The oxidation kinetics of the film and concurrent hydrogenation of nitrobenzene in hexane were measured. A satisfactory fit of the resulting kinetics was obtained using a model that involves two simultaneous processes. Kinetics of tungsten bronze oxidation follows a two-step mechanism involving a surface reaction with an oxidizing agent and diffusion of hydrogen from the bulk to the surface. The oxidation rates of the films depend on their

thickness, nature and concentration of the oxidant. Using the thickness dependence of the reaction rate, diffusion coefficient of H in WO₃ polycrystalline films was estimated to be approximately 10⁻¹³ cm²/s. The introduction of a catalyst onto the bronze surface is found to increase the reaction rate. Since the exact concentration of each element on the surface has not been determined, some caution should be exercised. However, the addition of catalytic amounts of various metal ions clearly increases the reaction rate and is an important area of future study.

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