Journal of Non-Crystalline Solids 409 (2015) 1–7

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Nature and distribution of tungsten oxides in porous Vycor glass

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ARTICLE INFO

Article history:
Received 26 July 2014
Received in revised form 1 November 2014
Accepted 6 November 2014
Available online 14 November 2014

Keywords:
Tungsten oxide;
Nanoporous silica;
Carbon dioxide

ABSTRACT

Tungsten oxides, including WO_3 and mixed valent oxides, are formed in unpolished porous Vycor glass (PVG) by ultraviolet photolytic decomposition of adsorbed tungsten hexacarbonyl. The relative amounts of the oxides formed are determined by a competition between aggregation and oxidation, and both are influenced by CO pressure gradients created by the photoinduced release of CO within the nanoporous silica matrix. These gradients sweep the hexacarbonyl precursor into the outer regions of the PVG, increasing amounts of tungsten nearer the surface, thereby enhancing the rate of aggregation relative to the rate of oxidation and promoting the formation of the mixed valent oxides. Thermolysis of the physisorbed hexacarbonyl, on the other hand, produces predominantly WO_3. Thermolysis promotes desorption of the physisorbed $W(CO)_6$, reducing the amount of tungsten available, permitting oxidation to be the predominant process over aggregation, leading to WO_3 formation.

1. Introduction

Interest in tungsten oxide nanoparticles dispersed in nanoporous silica stems from their photocatalytic [1–3] and optical applications [4–8]. Photopatterning an optical element in porous Vycor glass (PVG) involves four steps: physisorption of a photoactive metal carbonyl precursor into the silica matrix, photolysis of the adsorbed precursor, desorption of the unreacted precursor, and thermal consolidation of the matrix [9]. Photolysis decarbonylates the precursor which then undergoes oxidation creating metal oxide nanoparticles within the exposed volume. Thermal consolidation desorbs the unexposed precursor, consolidates the matrix, and incorporates the metal oxide nanoparticles into a nonporous, nonscattering silica glass thereby creating a region of higher refractive index than the bulk silica matrix. Although consolidation requires temperatures on the order of 1000 °C, surprisingly, consolidation yields refractive index patterns that guide, focus and diffract light [9–11]. A major challenge, however, is introducing addressable, active components capable of modifying the frequency, phase, polarization and/or coherence of the photons passing through the optical circuit. Silica glass is a refractory and its consolidation temperature, typically ≥1000 °C, limits the active reagents that can be incorporated into the matrix, and coupling these "optical chips" into a coherent network [9]. Transition metal oxides are capable of withstanding glass consolidation temperatures and introducing addressable physical properties such as magnetism, variable absorbance and reflectance into the optical network [9]. Tungsten and molybdenum oxides and their corresponding mixed valence oxides, for example, have been examined as electro- and photo-chromic materials for displays, smart windows, variable reflectance mirrors, and sensors [4–8].

UV photolysis of $W(CO)_6$ or $Mo(CO)_6$ physisorbed into PVG or structurally similar tetramethylorthosilicate/methanol/water (TMOS/MeOH/H_2O) xerogels also leads to metal oxides that photocatalyze the conversion of CO_2 to CH_4 [1–3]. Stoichiometric measurements, recovery of ≥98% of the coordinated CO, $^{13}C/^{12}C$ and H/D labeling, dependence on coabsorbed water, and the detection of 32–74% of the stoichiometrically expected O_2 establish that neither the zero valent tungsten or molybdenum photoproducts, nor the H_2 evolved from their oxidation by coadsorbed water are involved in the reduction of the CO_2. Rather, the hexacarbonyls are converted to metal oxides and one or more of the oxides promotes the evolution of CH_4 [1–3].

While there is considerable information on the initial photoinduced decarbonylation of the metal carbonyl precursors in solution and physisorbed into nanoporous silica matrices [12], there is little information on the oxidation of the zero valent photoproducts that actually create the optical structure or act as photocatalysts. The appearance of strong absorbance onsets in the general area of the MoO_3 and WO_3 band gaps, 2.6–3.0 eV [13–22] during photolysis, and their insensitivity to O_2 or air indicate the formation of WO_3 and MoO_3 [1]. Tungsten(VI) and molybdenum(VI) oxides are the thermodynamically expected oxides, and are detected under most conditions. However, other oxides are also formed. EPR spectra recorded during photolysis of $Mo(CO)_6$ads (ads is used throughout to designate the physisorbed complex), for example, reveal the presence of Mo(V) that is tentatively assigned to the hydrous oxide, MoO_2OH [23]. No EPR signal is detected during photolysis of $W(CO)_6$ads, but the stoichiometry of hydrogen evolution, 0.31 to 2.43 mol of H_2 evolved per mol of $W(CO)_6$ consumed, point to less than complete oxidation of some W atoms [12,23].

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http://dx.doi.org/10.1016/j.jnoncrysol.2014.11.005
0022-3093/

These experiments were undertaken to identify the tungsten oxides created photochemically in PVG, and the factors that influence their formation. With metal oxides derived from monometallic, metal carbonyl precursors, current data indicate that oxide formation within PVG and structurally similar TMOS/MeOH/H_2O xerogels is governed by a competition between oxidation and aggregation [24]. If the rate of oxidation exceeds the rate of aggregation, the dominant product is the fully oxidized metal, or with tungsten, WO_3. On the other hand, if the rate of aggregation exceeds the rate of oxidation, oxidation is limited to the outer atoms of the growing aggregate and mixed valence oxides are formed. Both rates are influenced by CO pressure gradients that develop within these nanoporous silicas during photolysis [25]. The high quantum efficiency of CO loss from the carbonyl precursor, and the relatively slow rate of CO diffusion from the interior of the silica matrix create CO pressure gradients within these nanoporous silica matrices. These pressure gradients "sweep" the physisorbed metal carbonyls from the interior of the matrix into the outer volumes [25]. As a result, photolysis and subsequent oxidation of the metal containing photoproducts occur under conditions quite different from those defined by the initial impregnation of the matrix by the metal carbonyl precursor. The surface coverage in the outer volumes of the matrices, for example, is rapidly increased thereby increasing the probability of aggregation. In addition, the enhanced rate of CO diffusion from the matrices more than likely decreases the amount of coadsorbed air and water which, as the major oxidants of the zero valent photoproducts, reduce the rate of oxidation in the outer volumes [25].

Tungsten oxides are defect structures that exhibit different tungsten/oxygen ratios, different crystallographic forms and different levels of crystallinity often in the same particle or aggregate [26–33]. To a significant extent, the specific oxide obtained depends on the method and details of the synthesis. Commercially available tungsten oxides, for example, are usually prepared by calcination of tungstic acid, H_2WO_4, or ammonium paratungstate tetrahydrate, $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$ (APT). In the presence of air, calcination yields yellow tungsten(VI) oxide, WO_3. In the absence of air, or under H_2 or NH_3 atmospheres, however, calcination leads to the formation mixed valence oxides that are collectively referred to as tungsten blue oxides (TBOs). TBO is a complex aggregate composed of crystalline and amorphous phases that contain, in addition to WO_3, differing amounts of tungsten bronzes, the β-oxide ($WO_{2.9}$ or $W_{20}O_{58}$), the γ-oxide ($WO_{2.72}$ or $W_{18}O_{49}$), and WO_2 [26–33].

Photolysis decarbonylates the hexacarbonyl precursor and the oxides formed in PVG are created by oxidation of the decarbonylated photoproducts. Stoichiometric measurements indicate oxidation initiates when the complex achieves an average stoichiometry of $W(CO)_4$ [3]. In the absence of a persistent, measurable absorbance attributable to $W(CO)_4$, the oxidation step does not appear to be photoassisted. Instead, whether the initial decarbonylation of the hexacarbonyl is initiated thermally or photochemically, the subsequent oxidation of the zero valent metal is a thermal process usually with coadsorbed water, ubiquitous in these nanoporous silicas, serving as the oxidant [24]. In spite of the different methods of preparation, i.e., oxidatively as opposed to reductively, the oxides formed in PVG are spectroscopically similar to the commercially available oxides. However, the distribution of oxides formed in PVG, a mixture of tungsten(VI) oxide with differing amounts of the mixed valence oxides, depends on the synthetic details. Thermolysis, for example, leads to a tungsten(VI) oxide with little to no mixed valence oxides, whereas photolysis leads to a mixture of tungsten(VI) oxide and mixed valence oxide aggregates containing both W(VI) and lower oxidation states of tungsten. The product distributions do not arise from differences in the amount of oxidant present. Instead the different product distributions arise from a chemistry determined by competition between oxidation and aggregation. Desorption of 70–80% of physisorbed $W(CO)_6$ during thermolysis reduces the rate of aggregation thereby leading to WO_3 as dominant oxide product, whereas larger amount of tungsten present in the matrix after photolysis favors a rate of aggregation competitive with oxidation. Indeed, electronic spectra and sensitivity to O_2 confirm that photolysis yields formation of two general classes of tungsten oxides in PVG. One is a small, ≤1 nm diameter, amorphous, hydrated oxide aggregate containing W^{6+} that converts to monoclinic WO_3 on heating. The other is a mixed valence aggregate containing tungsten in different oxidation states that spectroscopically resembles commercially produced TBO [26–33]. The relative amounts of the two classes of oxides formed depend on whether PVG is polished or not with the largest amount of the mixed valence oxide formed in the unpolished glass. The difference is not due to differences in PVG composition, surface hydroxylation, or differences in the physisorbed complex or its photochemical behavior. Rather, distribution measurements indicate photoinduced CO pressure gradients that redistribute the physisorbed hexacarbonyl such that the majority of the oxide formation occurs in the outermost 800–850 nm of the silica matrix. Since the outermost volumes of PVG are removed by polishing, the difference in the amounts of the fully oxidized and mixed valent tungsten oxides formed in the polished and unpolished PVG is attributed to structural differences, on a length scale of the correlation length of PVG, 22 ± 1 nm.

2. Experimental

2.1. Materials

$W(CO)_6$ (Alfa AESAR) was used as received since electronic spectra of hexane solutions of the complex agreed with published spectra. Unpolished, 2.54 cm × 2.54 cm × 4–5 mm, and polished, 2.54 cm × 2.54 cm × 2 mm, pieces of Corning's code 7930 porous Vycor glass (PVG) were extracted with distilled water for at least 48 h in a Soxhlet extractor and then dried in a vacuum desiccator at room temperature under reduced pressure. Some of the dried samples for thermolysis were heated to 625 °C for at least 24 h prior to use. The cleaned pieces were cooled to room temperature in a desiccator, and impregnated by a previously described solution impregnation procedure using a 0.01 M hexane solution of $W(CO)_6$ [1,3]. The amount of complex adsorbed, ca. 10^{-6} mol $W(CO)_6$ per gram of glass, was calculated from the changes in the absorption spectra of the impregnating solution. Hexane incorporated during impregnation was removed under vacuum at room temperature. Higher $W(CO)_6$ surface loadings were accomplished by adding as many as six drops of the 0.01 M $W(CO)_6$/hexane solution to each face of the sample and evaporating the solvent at room temperature under reduced pressure. This produced a loading of about 5×10^{-6} mol per gram of glass, but the majority of the adsorbed complex was in the outermost volume of the glass.

2.2. Photochemical and thermal procedures

The dried $W(CO)_6$ impregnated samples were mounted upright in previously described rectangular Pyrex or quartz cell and irradiated in air or under vacuum ($\leq 10^{-3}$ Torr) in a Rayonet reactor equipped with four 312-nm light bulbs [1,3]. Electronic spectra were recorded periodically during photolysis, and the extent of reaction was calculated from the decline in the 290 nm absorption of $W(CO)_6$ads. Some of the photolyzed samples were then heated in a Thermolyne 1500 muffle furnace at 625 °C for differing lengths of time and electronic spectra recorded periodically.

Thermolysis of the impregnated samples in air was examined in a similar manner. The $W(CO)_6$ impregnated samples were mounted upright in ceramic or Pt boats and placed in an open quartz tube in a Thermolyne 1500 muffle furnace at 625 °C for differing periods of time. The samples were removed periodically, electronic absorption spectra recorded, and then returned to the oven.