Deposition of Titanium-Vanadium Oxide Films on Organic Self-Assembled Monolayers

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Titania-supported vanadium oxide is an important heterogeneous catalyst in a variety of applications. Therefore, the synthesis of mixed titanium-vanadium oxide films may be of interest for potential thin-film catalysts. Titania and vanadia thin films can be individually deposited on organic self-assembled monolayers (SAMs) under similar conditions from aqueous solution. Specifically, anatase thin films can be deposited from 50 mN hexafluorotitanate solution at pH 2.88 at 50 °C on amine- and sulfonate-functionalized SAMs, and hydrated vanadia films can be deposited from 25 mN vanadate solution at pH 2.9 at 45 °C on amine- and alkylammonium-functionalized SAMs. With both titanium (50 mN) and vanadium (25 mN) ions present in the precursor solution, ~1:1 titania-vanadia hybrid amorphous films can de deposited on SAMs at pH 2.5-2.9 at 45 °C. However, although the single-oxide films show distinct preferences for certain surface functionalities (*i.e.*, titania films do not deposit on alkylammonium surfaces and vanadia films do not deposit on sulfonate surfaces), the mixed-oxide films grew to similar thicknesses (1.2-1.5 μm in 24 h) on both types of surfaces This suggests that the multicomponent films were formed via attachment of mixed (Ti,V)-oxide particles. Further details of the possible mechanism of deposition are discussed.
Key words: self-assembled monolayer (SAM), supported vanadium oxide, catalyst, titania

1. INTRODUCTION

The major non-metallurgical use of vanadium is in catalysis. Vanadium oxide-based catalysts are used in both oxidation reactions, *e.g.* SO_2 to SO_3 in the production of sulfuric acid[1,2], partial oxidation of methanol to formaldehyde[3], oxidation of butene to acetic acid[4], *et c.* and reduction reactions *e.g.* selective catalytic reduction of NO_x by NH_3 (SCR process)[5]. Titanium oxide is used not only as a support for vanadia-based catalysts, but as a catalyst itself *e.g.* for photocatalytic decomposition of organics[6]. In an extensive open literature search on transition metal oxide catalysts covering the period 1967-2000, 28% of the papers are on vanadium oxides and 15% are on titanium oxides.[7]

Most vanadium-based catalysts consist of a vanadium oxide phase deposited on the surface of an oxide support like TiO_2, Al_2O_3, SiO_2, ZrO_2, *et c.* Supported catalysts usually show higher activity due to a gain in surface area and mechanical strength. The supports were originally considered to be inert substances, which provide a high surface area to carry the active metal oxide component.[8] Recently, the properties of the support material were found to affect the activity and selectivity significantly (metal oxide-support effect). However, the exact origin and mechanism of operation is still unclear.

There are many methods for preparation of supported vanadium oxide catalysts, including wet impregnation[9,10], grafting[9,11-13], equilibrium adsorption[14-16], chemical vapor deposition (CVD)[17,18], atomic layer deposition (ALD)[19], sol-gel[20], and thermo spreading[21,22]. Almost all of these methods consist of dipping the supporting material (prepared separately) in a vanadium precursor environment.

In previous research, single-oxide titania and vanadia films were formed on organic self-assembled monolayers (SAMs) under similar conditions[23,24]. Selective deposition of each oxide was achieved through consideration of the electro-static interaction between colloid oxide particles and the surface functionality of various SAMs. Anatase thin films can be deposited from 50 mN hexafluorotitanate solution at pH 2.88, 50 °C, in 22 h, to thicknesses of 0.5 μm on amine SAMs and 1 μm thick on sulfonate SAMs. Hydrated vanadia films can be deposited from 25 mN vanadate solution at pH 2.9 at 25 °C in 24 h on to thicknesses of 1 μm on amine SAMs and 4 μm on alkylammonium SAMs. In the present work, with both vanadium and titanium ions present simultaneously in the precursor solution, mixed titanium-vanadium oxide films could be formed.

2. EXPERIMENTAL SECTION

2.1 General

NMR spectra are reported in units of δ and were recorded on a Varian XL-200 200 MHz spectrometer in $CDCl_3$ solvent. ^1H NMR spectra are referenced to $CHCl_3$ at 7.24 ppm. Dry THF and ether were distilled from Na. DMF was dried with anhydrous $MgSO_4$. All other chemicals were used as received.

Peak positions from x-ray photoelectron spectroscopy (XPS) were recorded on a PHI Model 5600 MultiTechnique system. XPS peaks were referenced to silicon 2p at 99.7 eV from the silicon single crystal (100) substrate. Sputtering-depth profiles were accomplished with a PHI 04-303 inert-gas sputtering source attached to the XPS. The gas used was 25 mPa ultra-pure argon with 4 kV

accelerating voltage, rastering over a 2 mm × 3 mm area in 1 min. The sputtering rate, calibrated against values of thickness determined from SEM cross-sectional images, was 1.79 nm s^{-1}. With the sputtering interval of 60 s, the built-in error in thickness was about 100 nm.

Grazing-incidence x-ray diffraction (GIXRD) traces were recorded with a Scintag Advanced Diffraction System with Cu Kα X-rays by fixing the X-ray source at 2° with a 1° sample tilt and varying the detector.

2.2 Synthesis of surfactant[23,25]

The trichlorosilane group is chemically reactive to electrophiles like amines. Therefore, it was necessary to start with a surfactant whose surface group was unreactive toward trichlorosilane, such as bromide (–Br). The bromide group was then replaced *in situ* after the initial bromide-terminated surface was established.

The procedure began with synthesis of ω-hexadecenyl bromide[26] from ω-undecenyl bromide (11.6 g, 50 mmol) via a Grignard reaction. The ω-hexadecenyl bromide was purified by distillation at 100-110 °C at 0.1 torr: yield 7 g (46%); ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.14-1.48 (m, 22H), 1.80 (m, 2H), 1.98 (m, 2H), 3.36 (t, J=7Hz, 2H), 4.88-5.04 (m, 2H), 5.80-5.92 (m, 1H). To add the trichlorosilane bonding group, ω-hexadecenyl bromide (1 g, 3.3 mmol), HSiCl$_3$ (5 mL), and 20 L of a 4% solution of H$_2$PtCl$_6$ in *i*-PrOH were added to a pressure tube under argon atmosphere in a dry box. The tube was sealed and held in an oil bath at 60 °C overnight. Excess HSiCl$_3$ was removed by distillation. The resulting 1-bromo-16-(trichlorosilyl)- hexadecane was purified by Kugelrohr distillation at 110-120 °C at 0.01 torr: yield 1.15 g (70%); ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.20-1.87 (m, 30H), 3.39 (t, J=7Hz, 2H).

2.3 Deposition of SAM

Substrates were p-type single-crystal (100) silicon wafers, polished on one side, cut to 1 cm by 1 cm. About 40 pieces were immersed in 100 mL of piranha solution (70 mL concentrated sulfuric acid (H$_2$SO$_4$) and 30 mL aqueous 30% hydrogen peroxide (H$_2$O$_2$) solution), then heated to 80 °C for 20 min. Thus oxidized and hydrolyzed (denoted here "Si-OH"), the substrates were rinsed three times and kept in distilled water until further use.

To form hexadecyl bromide-functionalized SAM surfaces (–C$_{16}$–Br), 24 pieces of Si-OH were immersed in a slowly stirred solution of surfactant (0.1 mL 1-bromo-16-(trichlorosilyl) hexadecane in 10 mL bicyclohexyl) at room temperature under argon in a dry box for 5 h.

2.4 In-situ transformations of monolayer functionality[23]

Unless otherwise noted, all SAM-coated substrates were washed with ethanol and dried with a stream of argon, and then thoroughly cleaned twice manually with fresh chloroform-soaked tissues until the surfaces were perfectly mirror-like. All the substrates were kept under argon in a dark place before use.

To form azide-functionalized surfaces[26] (–C$_{16}$–N$_3$), 12 pieces of –C$_{16}$–Br substrates were immersed in a slowly stirred solution of 0.2 g sodium azide (NaN$_3$) in 20 mL *N,N*-dimethylformamide at room temperature under argon in a dry box overnight.

To form primary-amine-functionalized surfaces

(–C$_{16}$–NH$_2$), 12 pieces of –C$_{16}$–N$_3$ substrates were immersed in a slowly stirred solution of 20 mL saturated lithium aluminum hydride (LiAlH$_4$) in diethyl ether at room temperature under argon in a dry box overnight. Each substrate was washed with 10% hydrochloric acid and then with ethanol, dried in a stream of argon, and then thoroughly cleaned twice manually with fresh chloroform-soaked tissues until the surfaces were perfectly mirror-like.

To form tertiary-amine-functionalized surfaces (–C$_{16}$–N(CH$_3$)$_2$), twelve –C$_{16}$–Br substrates were immersed in a slowly stirred solution of 10 mL aqueous 45% dimethylamine solution at room temperature overnight.

To form alkylammonium-functionalized surfaces (–C$_{16}$–N$^+$(CH$_3$)$_3$), two –C$_{16}$–N(CH$_3$)$_2$ substrates were immersed in 5 mL of slowly stirred dimethyl sulfate in a sealed pressure tube at 80 °C overnight.

To form thioacetate surfaces (–C$_{16}$–SCOCH$_3$), 12 pieces of –C$_{16}$–Br substrates were immersed in a slowly stirred solution of 0.7 g potassium thioacetate in 10 mL ethanol in a sealed pressure tube at 80 °C overnight.

To form sulfonate surfaces (–C$_{16}$–SO$_3$H), 12 pieces of –C$_{16}$–SCOCH$_3$ substrates were immersed in a slowly stirred solution of 30% H$_2$O$_2$ in acetic acid (1:5 v/v) at 50 °C for 1 h. To form cyanide surfaces (–C$_{16}$–CN), 4 pieces of –C$_{16}$–Br substrates were immersed in a slowly stirred solution of 0.5 g sodium cyanide in 10 mL dimethylsulfoxide (DMSO) solution in a sealed pressure tube at 80 °C overnight.

To form carboxylate-functionalized surfaces (–C$_{16}$–COOH), 4 pieces of –C$_{16}$–CN substrates were immersed in a slowly stirred solution of 0.5 g sodium bicarbonate in 10 mL distilled water in a sealed pressure tube at 40 °C for two days. Each substrate was washed with 1% hydrochloric acid and then with ethanol, dried with a stream of argon, and then thoroughly cleaned twice manually with fresh chloroform-soaked tissues until the surfaces were perfectly mirror like.

2.5 Deposition of Titanium-Vanadium Oxide Films

(NH$_4$)VO$_3$ 0.2925g (2.5 mmol) and boric acid 0.93 g (15 mmol) were dissolved in 80 mL distilled water at 80 °C. After the solution cooled to room temperature, (NH$_4$)$_2$TiF$_6$ 0.9890g (5 mmol) was added. The pH was adjusted to 2.5 by adding either 1N HCl or 1N NaOH aqueous solution dropwise. The whole solution was then diluted to 100 mL.

The SAM-coated substrates were immersed in this deposition solution. The dish was covered and then placed in an oil bath at 45 °C for 24 h. The coated samples were then rinsed with distilled water and dried with a stream of dry argon. The sample was then ultrasonically cleaned in absolute ethanol for 20 min.

3. Results and Discussion

3.1 Growth kinetics

Figure 1 shows the thickness of mixed V-Ti oxide films (determined from SEM cross-sectional images) deposited on alkylammonium-functionalized substrates as a function of immersion time. The growth rate was ~40 nm h^{-1} in the first 13 h of deposition but increased from 13 to 19 h. The average growth rate was 56 nm h^{-1} over 25 h. The data suggest a two-step growth process,

similar to that observed with vanadia films on alkylammonium SAMs[23]. In that work, $V_2O_5 \cdot 1.6H_2O$ grew at 1 μm h^{-1} in the first 24 h. After that, $V_2O_5 \cdot H_2O$ grew at a much faster rate of 2 μm h^{-1}. The similarities in growth kinetics between the vanadia and the vanadia-titania films further suggest that film growth involved a cooperation between vanadium and titanium ions.
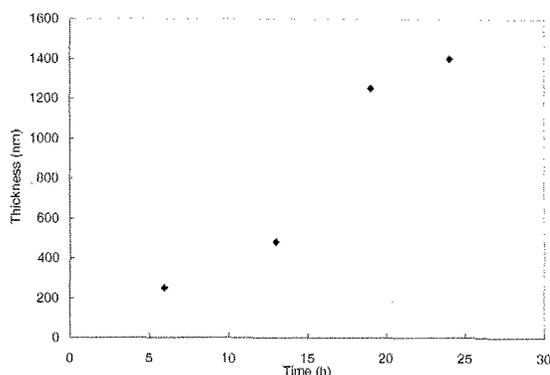
Figure 1. Growth kinetics of Ti-V oxide films on alkylammonium SAMs. Deposition conditions: [Ti] = 50 mN, [V] = 25 mN, 45 °C, pH = 2.5. Thickness determined from SEM cross-sections of films.

For different deposition times, the vanadium profiles overlapped with each other (Fig. 2). This means that there was no significant preferential sputtering between Ti and V. (The scatter in the data near zero thickness arises from the small amounts of Ti and V detected there.)
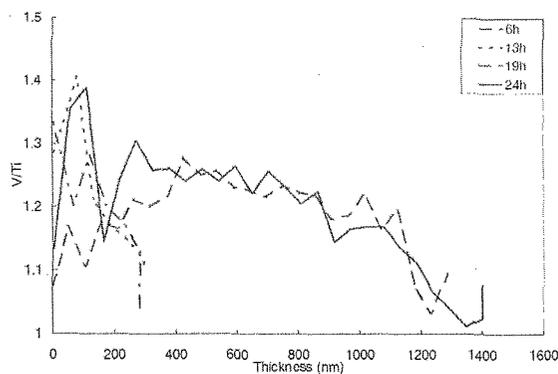
Figure 2. XPS V/Ti ratio from films with different deposition time. Deposition conditions as in Fig. 1

The films contained roughly equal atomic fractions of Ti and V (Figs. 2 and 3). This was true despite a V:Ti ratio of 1:2 in the deposition medium. The result may be due to slower reaction kinetics for metal halides (the Ti source was hexafluorotitanate ions) compared to metal oxides (the vanadium source was vanadate ions). Another explanation may be that the titania and vanadia species or nanoparticles may mutually attract due to their opposite charge in the deposition solution (pH 2.5) (Fig. 3). We now discuss this latter possibility.
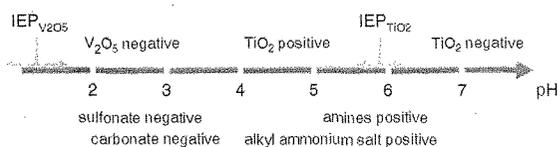
Figure 3. Surface charge of oxide particles and SAMs.

3.2 Substrate effects

Since vanadia and titania particles are negatively and positively charged, respectively, at pH 2~6, we hypothesized that charged surface functionalities on the substrate might attract certain species preferentially. For example, previous studies had shown that vanadia films deposit on positively charged amine and alkylammonium salt SAMs, but not on negatively charged sulfonate surfaces[23,27,28]. For acidic surfaces like sulfonate ($-SO_3H$) and carbonate ($-CO_2H$), a titanium-enriched film would be expected, whereas for positively charged surfaces like amine ($-NH_2$) and alkylammonium salt ($-N^+(CH_3)_3$), vanadium-rich films would be expected.
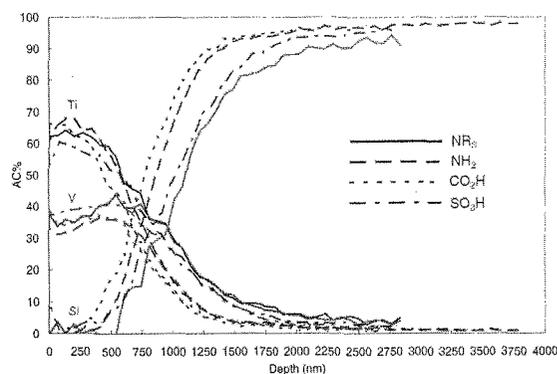
Figure 4. XPS depth profile of titania/vanadia film on Si substrate with different surface functionality. Deposition conditions as in Figure 1; deposition time = 24 h.

However, XPS sputter depth profiling showed the same Ti:V ratio regardless of the surface functionality (Fig. 4). The only difference between the different surface functionalities was that the more strongly charged surfaces (sulfonate and alkylammonium) yielded thicker films (1.5-1.8 μm, as determined from sputter depth profiling) than did the more weakly charged surfaces (amine and carboxylic acid) (1.2-1.5 μm) in 24 h of deposition. Unexpectedly, the sign of the surface charge had little or no effect in either case.

These results strongly suggest that the growth mechanism for these films involves attachment of existing particles (Fig. 5) rather than surface nucleation. That is, the hydrated vanadia and titania particles first formed in the aqueous solution and attracted each other due to their oppositely charged ionic double layers at the prevailing pH of 2.5. As a result, titania-vanadia aggregates formed with very little net surface charge. These particles were then attracted by a combination of van der Waals and induced dipolar/electrostatic forces to the substrate. The more highly charged SAM surfaces (sulfonate and alkylammonium salt) would induce stronger dipolar attractions, leading to the increase in film thickness. The films covered the substrates uniformly without cracks. In this respect they are similar to the pure vanadia films, which were also uncracked regardless of thickness up to

several micrometers; whereas pure titania films grown under similar conditions exhibit drying cracks when the thickness exceeds a few hundred nanometers[29]. Regardless of the substrate functionalization, the films were comprised of equiaxed particles ~60-100 nm in size (Fig. 6). No crystalline phases could be detected in any of these films using GIXRD.
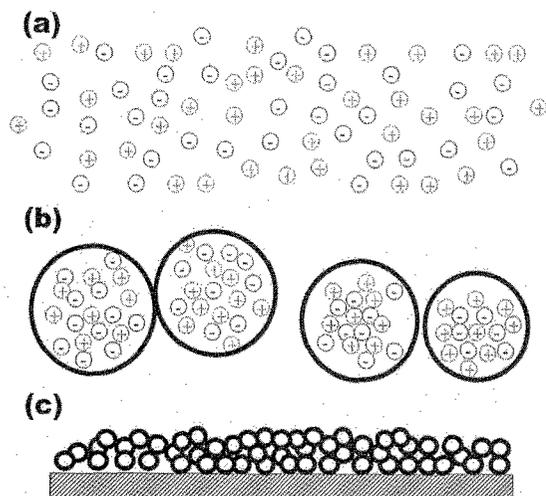
Figure 5. Proposed growth mechanism of Ti-V oxide thin films. (a) Titania (positively charged) and vanadia (negatively charged) formed in the solution. (b) Particles with opposite charge attract each other and form aggregates with little net surface charge. (c) SAMs induce polarization in aggregates and film formed.
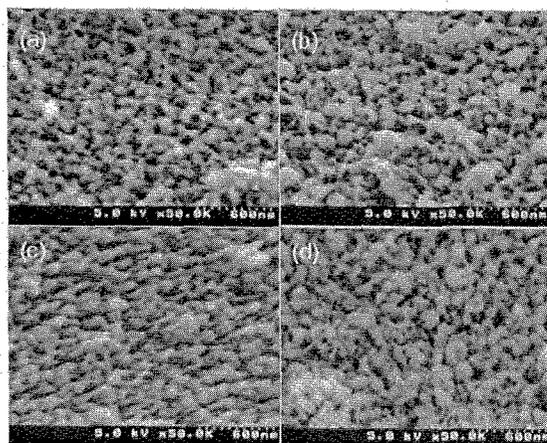
Figure 6. Topography of films deposited on SAMs. Deposition conditions as in Figure 1; deposition time: 24 h. a) $-SO_3H$; b) $-COOH$; c) $-NH_2$; d) $-N^+(CH_3)_3$.

4. Conclusions

Titanium-vanadium oxide films, synthesized with a view toward potential catalyst applications, were formed via co-deposition from aqueous solution on various SAMs. Unlike reported routes for preparing titania-supported vanadium oxide catalysts, the supporting material and active component can be prepared in one step.

Unexpectedly, the surface functionality of SAMs (the sign of the surface charge) had little or no effect on the film composition. Such a result strongly suggests that titania and vanadia particles formed mixed-oxide parti-

cles or aggregates in the solution with little net surface charge. These hybrid particles were then attracted by a combination of van der Waals and induced dipolar/electrostatic forces to the substrate to form the films.

5. References

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