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Reactivity of Monolayer V_2O_5 Films on $TiO_2(110)$ Produced via the Oxidation of Vapor-Deposited Vanadium

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Abstract

The growth, and reactivity of monolayer V_2O_5 films supported on $TiO_2(110)$ produced via the oxidation of vapor-deposited vanadium were studied using X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). Oxidation of vapor-deposited vanadium in 10^{-7} Torr of O_2 at 600 K produced vanadia films that contained primarily V^{+3} , while oxidation in 10^{-3} Torr at 400 K produced films that contained primarily V^{+5} . The reactivity of the supported vanadia layers for the oxidation of methanol to formaldehyde was studied using TPD. The activity for this reaction was found to be a function of the oxidation state of the vanadium cations in the film.

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Introduction

Vanadia supported on a second metal oxide such as titania is a highly active catalyst for a variety of selective oxidation reactions and the selective catalytic reduction of NO_x [1-6]. An important feature of supported vanadia catalysts is that the active form of the vanadia consists of a sub-monolayer or monolayer film on the surface of the oxide support [1,6-10]. In contrast, multilayer vanadia films and bulk V₂O₅ are relatively inactive. Although the structure of supported vanadia complexes is similar on a variety of oxide supports, interactions between the vanadia and the support have a dramatic effect on reactivity [3,7,11]. For example, Deo and Wachs have found that the turnover frequency (TOF) for the oxidation of methanol to formaldehyde on supported vanadia catalysts is a strong function of the identity of the support [7]. Although there have been numerous studies of these support effects, the mechanism by which the support influences the reactivity of the vanadia is still not completely understood.

Recently, in an effort to better understand the relationships between the structure and reactivity of supported vanadia catalysts several groups have studied model systems composed of vapor-deposited vanadia films supported on well-defined metal oxide single crystal surfaces including TiO₂(110) and CeO₂(111) [12-31]. In the studies of vanadia films on TiO₂(110) it has been found that vapor deposition of vanadium metal, either in the presence of a background of O₂ or followed by annealing in O₂, produces vanadia films that predominantly contain V⁺³ or mixtures of V⁺³ and V⁺⁴ for O₂ pressures less than 10⁻⁶ Torr [22,23,29]. The reactivity of these films has been studied using TPD of methanol [12,13]. For monolayer and submonolayer V₂O₃ coverages on TiO₂(110), formaldehyde is produced between 600 and 650 K during TPD with methanol-dosed

samples. Multilayer V_2O_3 films, however, have been found to be inactive for this reaction.

The catalytically active species in high surface area supported vanadia catalysts is generally thought to be a surface complex containing V^{+5} (i.e. V_2O_5). Thus, even though the studies of V_2O_3 films on $TiO_2(110)$ are interesting, they don't directly address the reactivity of the active species in industrial supported vanadia catalysts. In order to study the reactivity of more highly oxidized supported vanadia species, Wang and Madix have developed a method to grow monolayer films of V_2O_5 on $TiO_2(110)$ [17,18]. Their method relies on the hydrolysis of $VOCl_3$ and consists of co-dosing $VOCl_3$ and water at room temperature at a pressure of approximately 5×10^{-4} Torr followed by annealing in 2×10^{-6} Torr of O_2 at 600 K. These researchers found that during methanol TPD with a monolayer $V_2O_5/TiO_2(110)$ sample, formaldehyde was produced at 517 K. Note that this is roughly 100 K less than the temperature at which formaldehyde was produced on $V_2O_3/TiO_2(110)$ [12,13]. This result further demonstrates that V^{+5} is required for high activity for the oxidation of methanol to formaldehyde. Another interesting aspect of the Wang and Madix study is that once a V_2O_5 monolayer film was produced it was relatively easy to cycle the oxidation state of the vanadium cations between +5 and +3 [17,18]. It was shown that exposure of a monolayer $V_2O_5/TiO_2(110)$ sample to methanol at 450 K resulted in reduction of the vanadium cations from +5 to +3. Exposure of the reduced vanadia film to 2×10^{-6} Torr of O_2 at 600 K for 10 minutes was sufficient, however, to completely reoxidize the film. This result suggests that the structure of V_2O_3 films produced via reduction of $V_2O_5/TiO_2(110)$ differ from those of V_2O_3 films on $TiO_2(110)$ produced via oxidation of vapor deposited vanadium atoms.

Similar results have been obtained for monolayer and submonolayer vanadia films supported on CeO₂(111) [14]. In previous studies, we have shown that both V₂O₃ and V₂O₅ films supported on CeO₂(111) are active for the oxidation of methanol to formaldehyde. As was the case for monolayer vanadia films on titania, for the ceria-supported films the temperature at which formaldehyde is produced during methanol TPD depends on the oxidation state of the vanadium cations. On CeO₂-supported V₂O₃, formaldehyde was produced at 610 K, while on CeO₂-supported V₂O₅, formaldehyde was produced at 540 K.

One difference between the studies of V₂O₅/TiO₂(110) and V₂O₅/CeO₂(111) is the method used to grow the monolayer vanadia film. For the CeO₂(111) support it was found that V₂O₅ films could be synthesized by annealing vapor-deposited vanadium in 10⁻³ Torr of O₂ at 400 K. As noted above, in the previous studies of VO_x/TiO₂(110), annealing vapor-deposited vanadium in O₂ pressures up to 10⁻⁶ Torr did not produce fully oxidized vanadia and Wang and Madix had to resort to hydrolysis of VOCl₃ to produce films containing V⁺⁵ on this support. These results provide some evidence to support the idea that the substrate influences the ease of oxidation and/or the structure of the deposited vanadia layer. Alternatively in the case of TiO₂(110), the inability to produce V₂O₅ films via oxidation of deposited vanadium may merely be due to the fact that O₂ pressures higher than 10⁻⁶ Torr are required. We have investigated this possibility in the present study and have shown that V₂O₅ films on TiO₂(110) can indeed be produced via oxidation of vapor-deposited vanadium in 10⁻³ Torr of O₂. The reactivity of V₂O₅/TiO₂(110) samples produced in this manner has also been compared to those produced using the hydrolysis of VOCl₃.

Experimental

Experiments were conducted in 2 separate ultra-high vacuum (UHV) chambers. Both chambers were equipped with a mass spectrometer (UTI), a vanadium metal deposition source, a quartz crystal film thickness monitor (Maxtek), and an ion sputter gun (Physical Electronics). The chamber used for the TPD experiments was also equipped with a cylindrical mirror analyzer for Auger electron spectroscopy (AES). The chamber used for XPS contained an X-ray source (VG Microtech) and a hemispherical electron energy analyzer (Leybold-Heraeus).

The TiO₂(110) single crystal was obtained from Commercial Crystal Laboratories, and was mounted in a tantalum metal sample holder which was attached to a UHV sample manipulator. The temperature was monitored using a chromel-alumel thermocouple that was glued to the back surface of the TiO₂(110) sample. Heating was achieved via conduction from the tantalum holder, which could be heated resistively. The sample was cleaned using cycles of sputtering with 2 kV Ar⁺ ions and annealing at 800 K, until AES or XPS revealed little to no trace of impurities.

The vanadium metal source consisted of a tungsten filament that was wrapped with a piece of vanadium wire. The tungsten filament was heated resistively to a temperature sufficient to cause vaporization of the vanadium metal. The quartz crystal film thickness monitor was used to determine the amount of vanadium deposited. One monolayer of vanadium was defined to be 1.5×10^{15} atoms/cm² which is the density of vanadium atoms on the close packed V(110) surface. The sample was maintained at 300 K during all vanadium depositions. In order to produce a vanadium oxide layer, the sample was annealed in 10^{-7} or 10^{-3} Torr of O₂ following vanadium deposition. XP

spectra were collected using Al $K\alpha$ x-rays. The binding energy scale in the XP spectra was referenced to the Ti $2p_{3/2}$ photoemission peak of TiO_2 at 458.5 eV [32].

Methanol (Fisher, HPLC grade) was purified via repeated freeze-pump-thaw cycles prior to use and was admitted into the vacuum system using a variable leak valve. For TPD experiments, the sample was saturated with methanol at 300 K and then heated at a rate of 4.5 K/s. The mass spectrometer was multiplexed allowing multiple masses to be monitored simultaneously. Multiple m/e values were monitored during the TPD experiment to identify the products. These TPD curves have been corrected for overlapping cracking patterns and have been adjusted for the sensitivity factors of the mass spectrometer.

Results and Discussion

Figure 1 displays the O 1s and V 2p regions of XP spectra of the $TiO_2(110)$ surface, before and after deposition of 0.5 monolayers of vanadium, and after various oxidation treatments. Spectrum a in this figure corresponds to clean $TiO_2(110)$. The large peak centered at 529.8 eV is due to photoemission from the O 1s states. Note that satellite peaks at 518.0 eV and 520.0 eV, which result from the presence of the $K\alpha_3$ and $K\alpha_4$ X-rays in the non-monochromatic X-ray source, have been subtracted from the spectra. Spectrum b in Figure 1 was obtained after deposition of 0.5 ML of vanadium. In addition to the O 1s peak at 529.7 eV, the spectrum contains peaks centered between 510 and 517 eV, and 517 and 523 eV, which correspond to V $2p_{1/2}$ and V $2p_{3/2}$ states, respectively, of the deposited vanadium layer. The binding energies of the V 2p peaks are characteristic of the oxidation state of the vanadium cations. Values for the V $2p_{3/2}$

binding emerging for the various oxidation states of vanadium reported in literature are presented in Table 1 [33-39].

The V $2p_{3/2}$ peak in the spectrum of the as-deposited vanadium film (curve b, Figure 1) is very broad and as shown in the inset of the figure can be resolved into three peaks of roughly equal intensity centered at 512.3, 513.4, and 515.0 eV. For these curve fits, the full-width at half maximum (FWHM) of each peak was set to be the same as that of the O 1s peak. As shown in Table 1 these peak positions correspond to V^0 , V^{+2} , and V^{+3} , respectively. These results demonstrate that a portion of the deposited vanadium atoms have become oxidized to V^{+2} and V^{+3} by reaction with the $TiO_2(110)$ support. This result is consistent with previous studies of the vapor deposition of vanadium onto $TiO_2(110)$ [21,22].

Spectrum c in Figure 1 shows that annealing the as-deposited vanadium film in 10^{-7} Torr of O_2 for 1 hour at 600 K produces a significant change in the distribution of vanadium oxidation states. The V $2p_{3/2}$ region of the spectrum now contains a very broad peak centered at 515.1 eV. The inset shows that this feature can be resolved into four overlapping peaks centered at 512.3 (V^0), 513.4 (V^{+2}), 515.0 (V^{+3}), and 516.0 eV (V^{+4}). Based on the areas of fitted peaks, the relative abundance of each oxidation state is estimated to be 14, 23, 36, and 27 %, for V^0 , V^{+2} , V^{+3} , and V^{+4} , respectively. This result is consistent with NEXAFS and XPS studies by Biener et al [19], and Zhang and Henrich [22]. It is also similar to what has been reported for the growth of vanadia films on $CeO_2(111)$ using similar oxidation treatments [15].

Annealing the film in 10^{-3} Torr of O_2 at 400 K for 1 hour resulted in additional oxidation of the vanadia layer. After this treatment, the V $2p_{3/2}$ peak (spectrum d, Figure

1) was centered at 517.1 eV, which indicates that the majority of the vanadium cations were in the +5 oxidation state. The V 2p_{3/2} peak, however, is skewed slightly to lower binding energy, and as shown in the curve resolution in the inset some V⁺⁴ is still present in the film. This result is again similar to what has been reported for monolayer vanadia films on CeO₂(111) [15]. For simplicity, samples prepared in this manner will be referred to as V₂O₅/TiO₂(110) throughout the remainder of the paper.

Methanol TPD was used to probe the reactivity of monolayer V₂O₅/TiO₂(110) samples as a function of the oxidation treatment. Although monolayer vanadia coverage was used, it is possible that small regions of the TiO₂(110) support may still have been exposed. Therefore, in order to be able to distinguish between reactions occurring on the vanadia from those on the support, the reaction of CH₃OH on TiO₂(110) was initially studied. Methanol TPD experiments were conducted for a TiO₂(110) sample that had been pretreated by annealing in vacuum at 800 K for 30 minutes, and for a sample that had been exposed to 10⁻³ Torr of O₂ at 400 K for 1 hour. Both samples were found to be active for the oxidation of methanol to formaldehyde. As discussed below, however, the pretreatment conditions did have a significant effect on reactivity.

During a CH₃OH TPD experiments with the vacuum-annealed TiO₂(110) surface the only gaseous species detected were CH₃OH which desorbed in a broad feature between 300 and 700 K, and CH₂O which was produced in a small peak centered at 650 K. The CH₂O desorption curve for this sample is displayed in the upper portion of Figure 2. In a previous study, this formaldehyde peak has been attributed to the oxydehydrogenation of methoxide species formed via dissociative adsorption of methanol on surface oxygen vacancies [40].

The TiO₂(110) sample that was pretreated in oxygen was significantly more active than the vacuum-annealed sample for the oxidation of CH₃OH to CH₂O. During a CH₃OH TPD run with this sample CH₂O desorbed in a large peak centered at 660 K. Similar to the annealed TiO₂(110) sample, methanol also desorbed in a broad feature between 300 and 600 K, but a distinct peak could also be resolved at 660 K. The area of the formaldehyde peak from the oxygen-pretreated sample was roughly five times greater than that from the vacuum annealed sample. Similar results have been reported previously by both Henderson et al. [40] and Wang and Madix [18]. It has been suggested in these previous studies that oxygen adatoms are formed during exposure of the TiO₂(110) surface to O₂ and that these adatoms are responsible for the increased oxidation activity of the surface.

Methanol TPD data obtained from a 1 ML vanadia film on the TiO₂(110) support are displayed in Figure 3. The data in the upper panel of this figure were obtained from a V₂O₅/TiO₂(110) sample that was produced using the 10⁻³ Torr oxidation treatment. The CH₃OH desorption curve contains a narrow peak at the beginning of the run and a much larger and broader peak centered at 470 K. The former peak is most likely due to desorption of methanol from the sample support hardware. The tantalum sample holder heats up much more rapidly than the TiO₂(110) sample and this gives rise to the very abrupt leading edge of this peak.

Formaldehyde was produced in a relatively broad peak centered at 485 K. Note that this temperature is 175 K lower than the formaldehyde peak temperature obtained from the oxidized TiO₂(110) support. The area of the formaldehyde peak from the V₂O₅/TiO₂(110) sample was also approximately four times greater than that from the

oxidized $\text{TiO}_2(110)$ support. These differences allow the formaldehyde peak from the $\text{V}_2\text{O}_5/\text{TiO}_2(110)$ sample to be attributed to reaction on the vanadia film rather than reaction on the $\text{TiO}_2(110)$ support. In addition to CH_2O a small amount of H_2O and CO were also produced at 480 K during the TPD experiment.

Methanol TPD results obtained in a subsequent run are displayed in the lower panel of Figure 3. Note that the sample was not reoxidized between the first and second runs. Although the CH_3OH desorption curve for this sample is similar to that obtained from the freshly oxidized sample, the CH_2O desorption curve is significantly different. Formaldehyde appears in a small, broad peak centered at 615 K. The area of this peak is only 12% of that obtained from the freshly oxidized $\text{V}_2\text{O}_5/\text{TiO}_2(110)$ sample. No other gaseous products were detected in this experiment. As noted in the introduction we have previously studied the reaction of methanol on monolayer V_2O_3 films on $\text{TiO}_2(110)$ [12,13]. In that study it was found that formaldehyde was produced between 600 and 650 K during CH_3OH TPD. Thus, the shift of the CH_2O peak to higher temperatures in the second run can be attributed to reduction of the vanadia layer during the first TPD run. A similar trend has also been reported for the oxidation of methanol to formaldehyde on vanadia films supported on $\text{CeO}_2(111)$ [14].

As was the case in the present work, previous studies of vanadia films on both $\text{TiO}_2(110)$ [17] and $\text{CeO}_2(111)$ [15] have shown that it is difficult to synthesize fully oxidized vanadia films on these surfaces under high vacuum conditions. It has been reported that much less stringent oxidation treatments are needed to reoxidize a V_2O_3 film that was produced via reduction of a V_2O_5 film than to fully oxidize a freshly deposited vanadium layer. Therefore, the reoxidation of partially reduced vanadia films

on $\text{TiO}_2(110)$ was also investigated in the present study. In this series of experiments the oxidation treatment was varied in order to determine the conditions required to produce a fully oxidized vanadia layer. The temperature at which formaldehyde was produced during a methanol TPD run was used as a chemical probe of the oxidation state of the vanadium cations. The results of this series of experiments are presented in Figure 4.

The bottom CH_2O desorption spectrum in Figure 4 is the same as that in the lower half of Figure 3 and was obtained from a $\text{V}_2\text{O}_5/\text{TiO}_2(110)$ sample that had been reduced by a preceding CH_3OH TPD run. This sample was then exposed to 10^{-6} Torr of O_2 at 300 K for 10 min. In the subsequent CH_3OH TPD run, the formaldehyde peak was centered at 585 K. The area of the peak also increased relative to that obtained from the reduced sample. Although the downward shift in the peak position suggests some reoxidation of the vanadia layer, +3 still appears to be the predominate oxidation state of the vanadium cations.

Curves c through e in Figure 4 were obtained from samples that were reoxidized in 10^{-3} Torr of O_2 at 300 K for 30, 600, and 3600 secs, respectively. The CH_2O desorption spectrum from the sample that was reoxidized for 30 secs contains a large and broad peak spanning from 370 to 700 K. The width of the peak suggests that the vanadia film contains a range of oxidation states. Increasing the duration of the 10^{-3} Torr O_2 exposure caused the CH_2O peak to sharpen considerably and shift to lower temperature. Following the 3600 sec exposure the CH_2O peak was centered at 480 K with a broad tail to higher temperatures. This peak temperature is the same as that obtained from a freshly prepared $\text{V}_2\text{O}_5/\text{TiO}_2(110)$ sample and indicates that the film contained V^{+5} . The tail to higher temperature, however, demonstrates that the film is not fully oxidized and still

contains a significant amount of V^{+4} and V^{+3} . In a separate set of experiments it was found that temperatures in excess of 400 K and O_2 pressures of at least 10^{-3} Torr were required during the re-oxidation step in order to obtain a sample that exhibited methanol TPD results identical to those obtained from a freshly prepared $V_2O_5/TiO_2(110)$ sample.

It is interesting to compare the results obtained in the present study with those reported previously by Wang and Madix [17,18]. As noted above, Wang and Madix used CH_3OH TPD to characterize the reactivity of vanadia films on $TiO_2(110)$ that were synthesized via the hydrolysis of adsorbed $VOCl_3$. This synthesis route appears to have the advantage of being able to produce films that contain exclusively V^{+5} . In contrast, in the present study vanadia films that were produced by annealing vapor-deposited vanadium in 10^{-3} Torr of O_2 always contained a small amount V^{+4} in addition to V^{+5} . In both studies the temperature at which adsorbed methoxy intermediates underwent dehydrogenation to produce CH_2O was found to depend on the oxidation state of the vanadium cations in the monolayer film. More fully oxidized vanadia was found to be more active for this reaction and CH_2O was produced at significantly lower temperatures on films that contained predominantly V^{+5} relative to those that contained predominantly V^{+3} .

Although there are many similarities between the results obtained in this study and those of Wang and Madix there are also some potentially important differences. For example, the CH_2O peak temperature during methanol TPD with monolayer $V_2O_5/TiO_2(110)$ samples varied between the two studies. Wang and Madix observed that CH_2O was produced at 517 K [17,18], while this reaction occurred at 480 K in the present study. This difference is too large to be attributed to uncertainties in the

temperature measurements in the two studies. The fact that the CH₂O peak temperature during CH₃OH TPD on oxidized TiO₂(110) surfaces was nearly identical in the two studies also indicates that for V₂O₅/TiO₂(110) the difference in the CH₂O peak temperature is significant.

The ease of reoxidation of a monolayer vanadia film following a CH₃OH TPD experiment also varied between the two studies. Wang and Madix report that the VOCl₃ derived V₂O₅ films could be reoxidized following a TPD run by annealing in 2x10⁻⁶ Torr of O₂ at 600 K for 10 minutes [17,18]. In contrast, more stringent oxidation treatments were required in the present study and O₂ pressures of at least 10⁻³ Torr were needed to both initially form the V₂O₅ film and to reoxidize it following a TPD run. These results provide additional evidence that there is something fundamentally different about a monolayer V₂O₅ film on TiO₂(110) produced by hydrolysis of adsorbed VOCl₃ and one produced by the oxidation of vapor-deposited vanadium. It is possible that the two synthesis routes produce films with different structures. Detailed studies of film structure as a function of the synthesis conditions are needed, however, in order to show that this is indeed the case.

Conclusions

In this study it was shown that vanadia films containing predominantly of V⁺⁵ can be grown on TiO₂(110) by oxidizing vapor-deposited vanadium metal in 10⁻³ Torr of O₂ at 400 K. During TPD with methanol-dosed VO_x/TiO₂(110) samples, adsorbed methoxide intermediates underwent dehydrogenation to produce formaldehyde. The temperature at which this reaction takes place was found to be a function of the oxidation

state of the vanadium cations. On films that contained predominantly V^{+3} , CH_2O was produced at 615 K, while on films that contained predominantly V^{+5} CH_2O was produced at 485 K. Finally, it was shown that the synthesis procedure for V_2O_5 films on $TiO_2(110)$ influences their reactivity. On V_2O_5 films produced via oxidation of vapor-deposited vanadium, dehydrogenation of adsorbed methoxides to produce formaldehyde occurs at 485 K, while this reaction proceeds at 517 K on V_2O_5 films produced via the hydrolysis of $VOCl_3$. This result along with the observation of differences in the ease of reoxidation of the films also suggests that the structure of the V_2O_5 film is dependent on the synthesis procedure.

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Table 1
V 2p_{3/2} binding energies

Compound	Vanadium Oxidation State	V 2p _{3/2} (eV)	Ref.
V	0	512.3±0.4	[33-36]
VO	+2	513.1±0.6	[34,37]
V ₂ O ₃	+3	515.3±0.3	[33,37-39]
VO ₂	+4	515.7±0.3	[33,36-39]
V ₂ O ₅	+5	516.8±0.2	[33,35,36,38,39]

Figure Captions

- Figure 1. XP spectra of the V 2p and O 1s regions for (a) clean TiO₂(110), (b) TiO₂(110) following deposition of 0.5 ML of vanadium, (c) after exposing the sample in b to 10⁻⁷ Torr of O₂ at 600 K for 1 hour, and (d) after exposing the sample in c to 10⁻³ Torr of O₂ at 400 K for 1 hour. A magnified view of the V 2p_{3/2} peaks with curve fits is shown in the inset.
- Figure 2. CH₂O desorption curves obtained during CH₃OH TPD runs with annealed TiO₂(110), and TiO₂(110) oxidized in 10⁻³ Torr of O₂.
- Figure 3. CH₂O and CH₃OH desorption curves from 2 consecutive CH₃OH TPD runs with a 1 ML V₂O₅/TiO₂(110) sample. The sample was not reoxidized between the runs.
- Figure 4. CH₂O desorption curves from a CH₃OH TPD experiment with a reduced 1 ML V₂O₅/TiO₂(110) sample that have been reoxidized in various amounts of O₂.

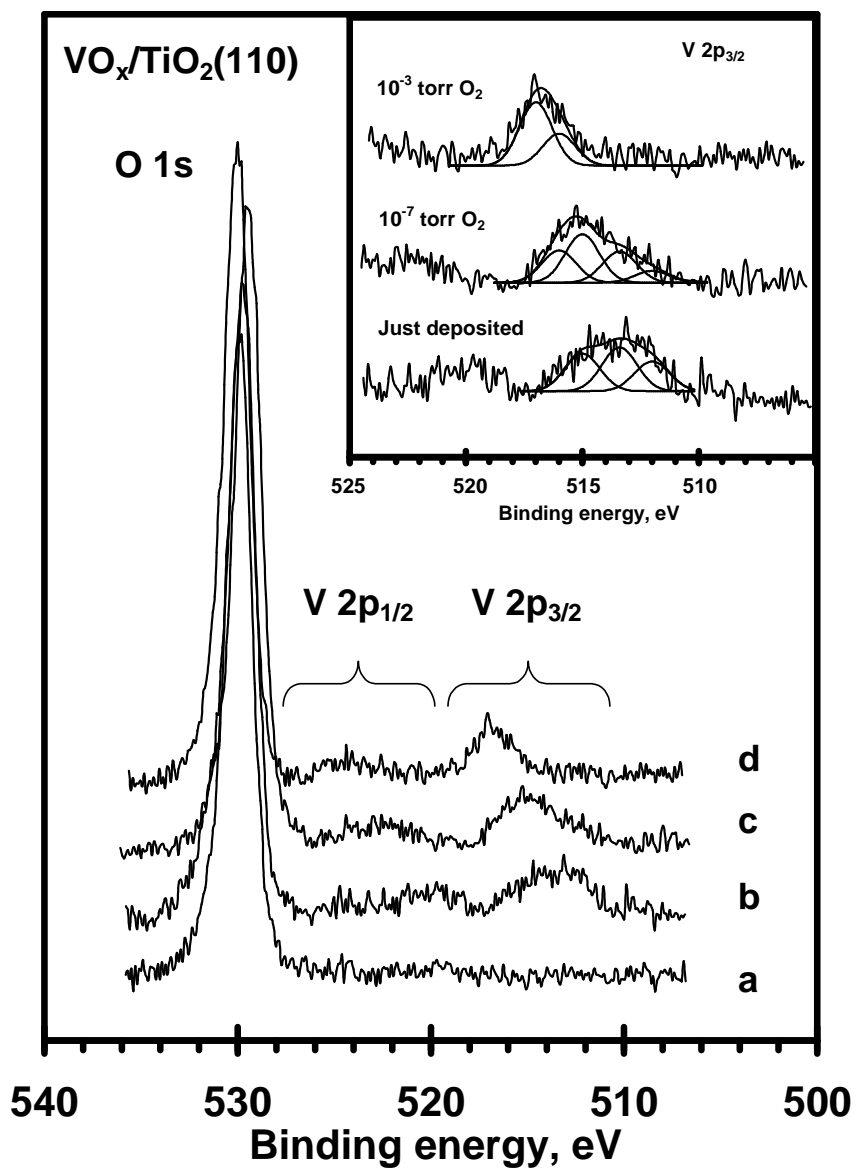


Figure 1

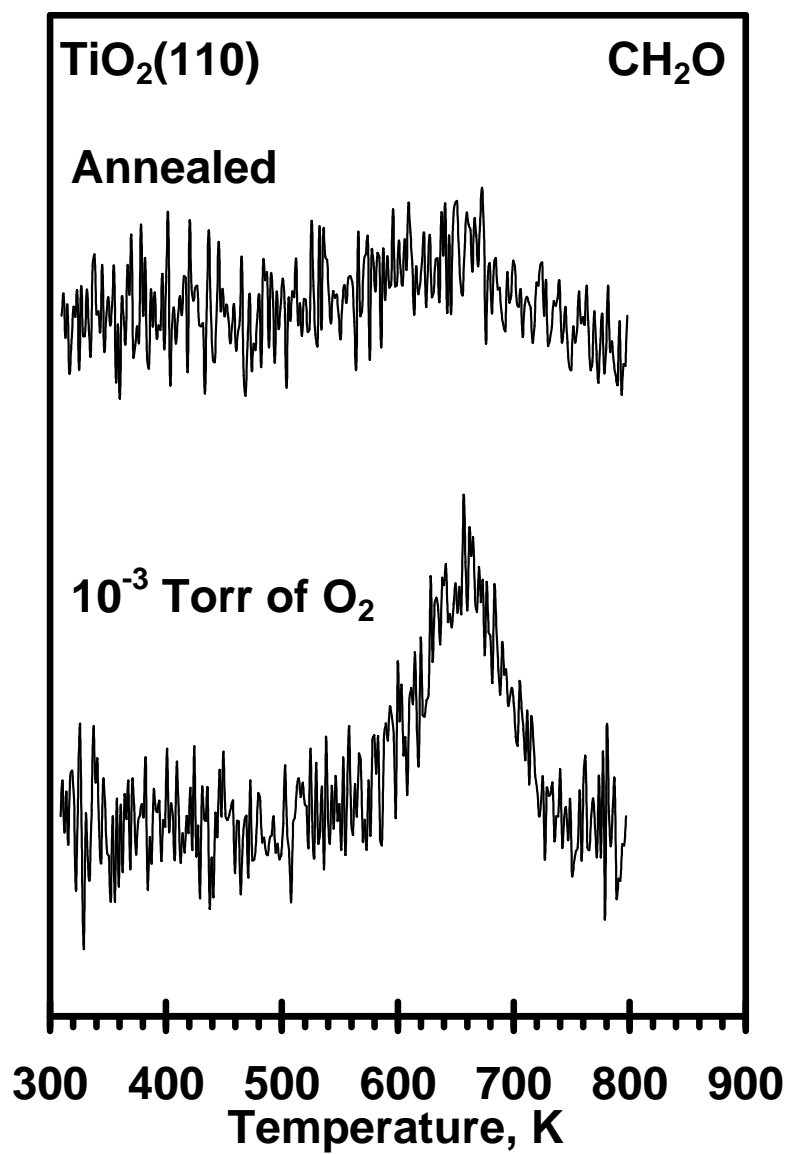


Figure 2

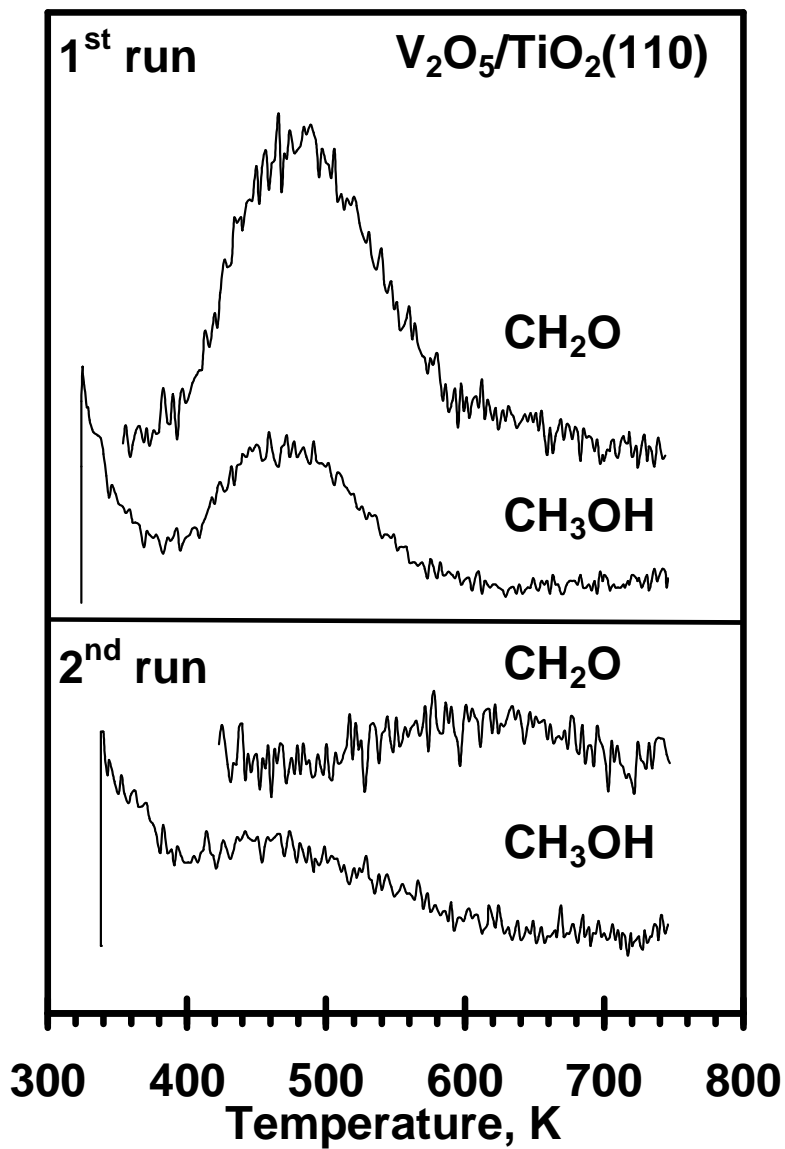


Figure 3

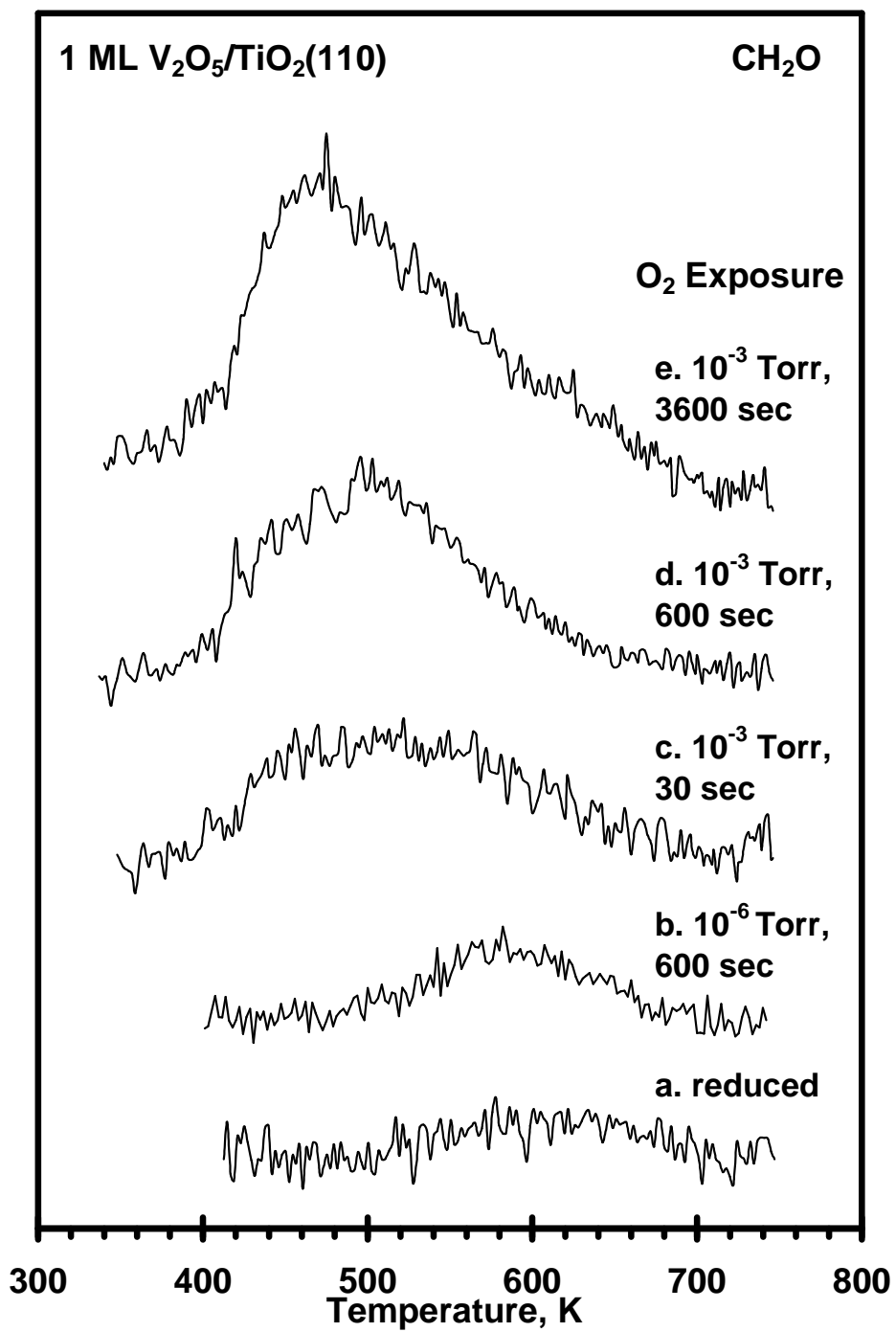


Figure 4