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Comparison of the reactivity of high-surface area, monolayer vanadia/ceria catalysts with vanadia/CeO_2(1 1 1) model systems

J. M. Vohs*, T. Feng, G. S. Wong

Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104-6393, USA

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Abstract

In this study, temperature programmed desorption (TPD) was used to compare the reactivity of a high-surface area, monolayer vanadia/ceria catalyst with that of a 0.5 ML ceria film supported on the (1 1 1) surface of CeO_2 single crystal. TPD and X-ray photoelectron spectroscopy (XPS) experiments with the vanadia/CeO_2(1 1 1) model system were carried out in an ultra-high-vacuum surface analysis system, while TPD studies for the high-surface area vanadia/ceria catalyst were conducted in a high-vacuum microbalance equipped with a mass spectrometer. The TPD studies showed similar reactivity for both samples. They were both active for the oxidation of methanol to formaldehyde and the temperature at which adsorbed methoxide intermediates underwent dehydrogenation to produce formaldehyde during TPD was found to be a function of the oxidation state of the cations in the supported vanadia layer for both samples. The similarity in the results obtained in this study from the high and low surface area samples indicates that monolayer vanadia films supported on metal oxide single crystals are excellent models of high-surface area, polycrystalline, supported vanadia catalysts.

Keywords: Vanadium oxide; Cerium oxide; Temperature programmed desorption; X-ray photoelectron spectroscopy; Oxidation; Alcohols

1. Introduction

Vanadium oxide supported on a second oxide such as TiO_2, CeO_2, or ZrO_2 is an active catalyst for a variety of reactions including selective oxidations, such as methanol to formaldehyde and *o*-xylene to phthalic anhydride, and the selective catalytic reduction (SCR) of NO_x with ammonia [1–3]. These catalysts are often referred to as monolayer supported oxide catalysts due to the fact that monolayer and submonolayer films of vanadia exhibit higher activity and selectivity than the unsupported oxide.

Much effort has been directed towards characterizing the structure of supported vanadia catalysts [4–12]. Based primarily on Raman studies it has been shown that the supported vanadia complexes consist of isolated vanadyls or polymeric vanadates with terminal V=O bonds [2,13–17]. It has also been shown that the structure of supported vanadia monolayers is largely independent of the specific oxide support [13,14]. In light of this observation it is very interesting that the support has a strong influence on the overall reactivity. For example, the turnover frequency for the oxidation of methanol to formaldehyde varies

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* Corresponding author. Tel.: +1-215-8986318; fax: +1-215-5732093.
E-mail address: vohs@seas.upenn.edu (J.M. Vohs).

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by several orders of magnitude for the following supports: Al_2O_3, Nb_2O_5, TiO_2, ZrO_2, CeO_2 [18].

Recently in an attempt to provide a more detailed understanding of the relationships between the structure and activity of supported vanadia catalysts and the role of the vanadia–support interactions, several groups including ours have studied model catalysts consisting of vanadia films supported on metal oxide single crystal surfaces [19–28]. The advantage of this approach is that it facilitates the use of a wide range of surface spectroscopic and structural probes to characterize the vanadia films. For these surface science studies to be successful and provide new insight into structure–activity relationships for high-surface area supported vanadia catalysts it is important that connections can be made between the insights obtained from the single crystal model systems and the corresponding high-surface area analogs. In order to achieve this goal we have been doing extensive temperature programmed desorption (TPD) studies of high-surface area supported vanadia catalysts in parallel with our studies of single crystal model systems. In this paper, we compare results obtained in studies of the reactivity of a vanadia monolayer supported on $CeO_2(1\,1\,1)$ with those obtained from a high-surface area ceria/vanadia catalyst. The results of this study demonstrate that single crystal, supported monolayer vanadia films are indeed excellent model systems for the real world catalyst.

2. Experimental

2.1. Vanadia/$CeO_2(1\,1\,1)$ model catalysts

The experimental studies of the reactivity of vanadia films supported on the (1 1 1) surface of a CeO_2 single crystal made use of two separate ultra-high-vacuum (UHV) surface analysis system. One system was used primarily for TPD measurements while the other was used for X-ray photoelectron spectroscopy (XPS) analysis. The TPD system was equipped with a mass spectrometer (UTI), ion sputter gun (Physical Electronics), quartz crystal film thickness monitor (Maxtek), cylindrical mirror electron energy analyzer (Omicron) for Auger electron spectroscopy (AES), and an evaporative vanadium metal source. The XPS system was equipped with an X-ray source (VG Microtech) and hemispherical electron energy analyzer (Leybold-Heraeus), sputter ion gun (Physical Electronics), quartz crystal film thickness monitor (Maxtek), and an evaporative vanadium metal source. The background pressure in each analysis chamber was $\sim 2 \times 10^{-10}$ Torr.

The $CeO_2(1\,1\,1)$ single crystal used in this study was obtained from Commercial Crystal Laboratories and was mounted in a tantalum metal sample holder which was attached to the UHV sample manipulator. The temperature was monitored using a chromel–alumel thermocouple which was glued to the back surface of the $CeO_2(1\,1\,1)$ crystal using a ceramic adhesive. The sample was heated resistively by passing an electrical current through the tantalum sample holder. Prior to vanadia film growth, the $CeO_2(1\,1\,1)$ sample was cleaned using cycles of sputtering with 2 kV Ar^+ ions and annealing at 750 K.

The evaporative vanadium metal sources, which consisted of a tungsten filament wrapped with a piece of vanadium wire, were used to deposit vanadium films on the $CeO_2(1\,1\,1)$ substrate. The quartz crystal film thickness monitors were used to determine the amount of vanadium deposited. In order to produce a vanadium oxide layer, the sample was annealed in 10^{-7}–10^{-3} Torr of O_2 following vanadium deposition.

XP spectra were obtained using Al Kα X-rays. The binding energy scale in the XP spectra was referenced to the primary $3d_{5/2}$ photoemission peak of the Ce^{4+} cations in the $CeO_2(1\,1\,1)$ support which occurs at 916.96 eV [29,30]. Satellites of the O 1s peak resulting from photoemission excited by Al Kα_3 and Kα_4 X-rays were subtracted from the O 1s/V 2p spectra using standard techniques.

Methanol (Fisher, HPLC grade) was purified using repeated freeze–pump–thaw cycles prior to use and was admitted into the vacuum system using a variable leak valve. For the UHV TPD experiments, the vanadia/$CeO_2(1\,1\,1)$ sample was dosed with 20 l of methanol at 300 K and then heated at a rate of 4.5 K/s. The TPD curves presented below have been corrected for overlapping cracking patterns and scaled to account for differences in the sensitivity factors for each product.

2.2. High-surface area, polycrystalline vanadia/ceria

The high-surface area ceria support used in this study was synthesized by decomposing $Ce(NO_3)_3$

(99.5% pure, Alfa Aesar) in air at 875 K. The surface area of the resulting ceria, as measured using the BET method, was 35 m^2/g. The incipient-wetness technique was used to deposit vanadia on the ceria support. This was done using an aqueous solution of ammonium metavanadate (NH_4VO_3, Sigma) and oxalic acid ($C_2O_4H_2$, Aldrich) in a 2:1 molar ratio. The concentration of vanadate and the total amount of impregnation solution was adjusted in order to produce catalyst with vanadia weight loading of 8%, which corresponds to slightly more than monolayer coverage. After impregnation of the vanadate, the sample was dried overnight at 400 K and then calcined in air at 775 K for 5 h.

TPD experiments with the high-surface area vanadia/ceria catalyst were performed using a vacuum microbalance (Cahn) equipped with a mass spectrometer (VG Scientifics). A 30 mg sample of the catalyst was placed in the sample pan, attached to the microbalance and then enclosed in a quartz thimble. The system was evacuated using a diffusion pump. A tube furnace placed around the quartz thimble, which housed the sample, was used to heat the sample radiantly. The temperature was monitored using a thermocouple placed inside the tube furnace, but external to the vacuum system.

After evacuating the system, the sample was heated to 475 K in order to remove any adsorbed water, surface hydroxyls, and other weakly adsorbed impurities. In a TPD experiment, the sample was exposed to ~15 Torr of methanol (Fisher, HPLC grade) vapor at room temperature. The exposure time varied somewhat from run to run but was long enough to ensure that the sample was saturated with methanol as determined by a leveling off of the weight gain. The system was then evacuated and once the pressure had returned to the baseline of ~10^{-7} Torr, a TPD experiment was performed. A heating rate of 15 K/min was used in each TPD run.

3. Results and discussion

Since the data obtained from the model vanadia/$CeO_2(1\,1\,1)$ sample are very useful in explaining the results obtained from the high-surface area catalyst, this data will be presented first. Fig. 1 displays the O 1s and V 2p regions of the XP spectra obtained following deposition of 0.5 ML of vanadium on the $CeO_2(1\,1\,1)$ support and several different oxidation treatments. The spectrum of the clean $CeO_2(1\,1\,1)$ support (spectrum a) is also included in the figure for comparison. The large peak centered at 529.6 eV in all the spectra corresponds to the O 1s electrons of both the ceria and the supported vanadia layer. Spectrum b was obtained following deposition of 0.5 ML of vanadium. The broad features centered at 515.7 and 523.2 eV are due to the V $2p_{3/2}$ and V $2p_{1/2}$ states, respectively. The binding energies of the V 2p peaks are a function of the oxidation state of the vanadium atoms. Based on data in the literature, the V $2p_{3/2}$ peak for V^{3+} cations has a binding energy of 515.7 eV. Thus, the position of the V $2p_{3/2}$ peak in the spectrum of the as-deposited 0.5 ML film is consistent with V^{3+}. The rather broad nature of the V 2p doublet, however, suggests that cations with other oxidation states are also present in the film. Since oxygen was not present in the gas phase during vanadium deposition, oxidation of the deposited vanadium atoms must have occurred via reaction with the ceria support. In a more detailed XPS study of this system

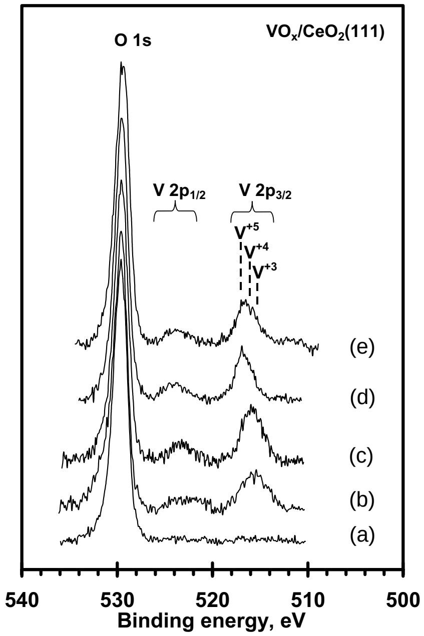

Fig. 1. O 1s and V 2p XP spectra for (a) clean $CeO_2(1\,1\,1)$, (b) $CeO_2(1\,1\,1)$ following deposition of 0.5 ML of vanadium, (c) after exposing the sample in (b) to 10^{-7} Torr of O_2 at 550 K for 1 h, (d) after exposing the sample in (c) to 10^{-3} Torr of O_2 at 400 K for 1 h and (e) after heating a 0.5 ML $V_2O_5/CeO_2(1\,1\,1)$ sample to 750 K.

that has been reported previously [22], it was shown that this is indeed the case and that oxidation of the deposited vanadium is accompanied by partial reduction of the $CeO_2(1\,1\,1)$ surface. It was also shown in that study that the vanadia film grows in a layer-by-layer fashion on this surface.

Spectra c and d in Fig. 1 show the effect of two different oxidation treatments on the oxidation state of vanadium atoms in the supported layer. Annealing in 10^{-7} Torr of O_2 for 1 h at 550 K (spectrum c) produced a decrease in the width of the V $2p_{1/2}$ and $2p_{3/2}$ peaks, but they remained centered at the same binding energies as those in the spectrum of the as-deposited film. Thus, the vanadium cations are predominantly in the +3 oxidation state after this oxidation treatment. Annealing in 10^{-3} Torr of O_2 for 1 h at 400 K (spectrum d) caused the V 2p doublet to shift to higher binding energies. After this treatment the V $2p_{3/2}$ peak was centered at 516.9 eV which is indicative of V^{5+} [31,32]. For simplicity, films subjected to this oxidation treatment will be referred to as V_2O_5 throughout the remainder of the paper.

Spectrum e in Fig. 1 was obtained after heating a $V_2O_5/CeO_2(1\,1\,1)$ sample to 750 K. Note that the V 2p doublet has shifted back to lower energy. The V $2p_{3/2}$ peak is now centered at 516.2 eV and slightly skewed toward lower binding energies. This change is indicative of partial reduction of the V_2O_5 film. Based on the peak shape and position, this film most likely contains a mixture of V^{5+}, V^{4+}, and V^{3+} cations.

The oxidation of methanol to formaldehyde was used to probe the reactivity of the supported vanadia catalysts. Methanol TPD results for a vanadia/$CeO_2(1\,1\,1)$ sample are presented in Fig. 2. The upper panel in this figure was obtained from a V_2O_5/$CeO_2(1\,1\,1)$ sample that was prepared by annealing in 10^{-3} Torr of O_2 at 400 K and then briefly flashed in vacuum to 500 K. The primary desorbing species during TPD were CH_3OH and CH_2O both of which appeared in peaks centered at 540 K. Small amounts of CO, CO_2 and H_2O were also produced at temperatures between 400 and 550 K but are not shown in the figure. This result demonstrates that the supported, submonolayer V_2O_5 film is active for the selective oxidation of methanol to formaldehyde. Note that it has previously been shown that multilayer vanadia films on $CeO_2(1\,1\,1)$ are not active for this reaction [19].

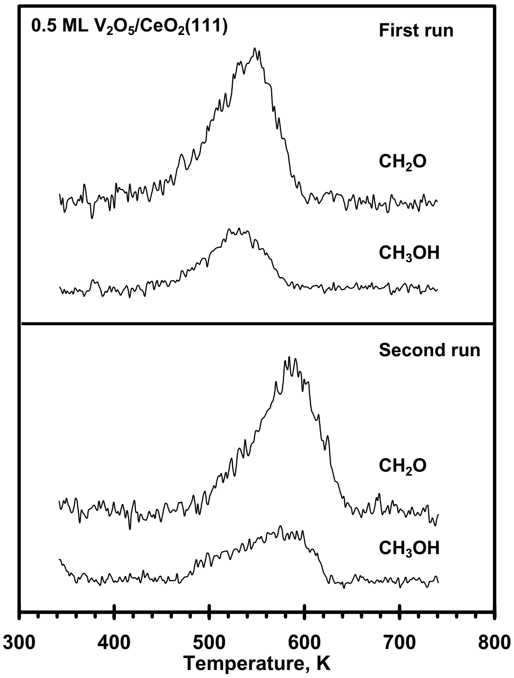

Fig. 2. CH_2O and CH_3OH desorption spectra obtained from a CH_3OH-dosed 0.5 ML V_2O_5 film on $CeO_2(1\,1\,1)$. The upper panel displays spectra obtained in the first run with a freshly prepared sample and the lower panel displays spectra obtained in the subsequent run.

The CH_3OH TPD data displayed in the lower panel in Fig. 2 were obtained immediately following those in the upper panel. As noted above, heating the sample to 750 K causes partial reduction of the vanadia film. This in addition to the fact that some water is produced during a CH_3OH TPD run ensures that the sample used in the second TPD experiment was highly reduced and contains predominantly V^{3+}. Note that while CH_3OH and CH_2O were again the primary desorbing species, for this reduced sample the peak temperatures are significantly higher than those obtained from the $V_2O_5/CeO_2(1\,1\,1)$ sample. For the reduced sample, CH_2O and CH_3OH both desorbed in peaks centered at 590 K. These results are consistent with those reported previously by our group [19] and demonstrate that the activation energy for the dehydrogenation of adsorbed methoxide intermediates to produce formaldehyde is a function of the oxidation state of the cations in the vanadia film. On monolayer V_2O_3 films (i.e. films that contain V^{3+})

dehydrogenation of methoxide to formaldehyde occurs at 590 K, while this reaction occurs at 540 K on monolayer V_2O_5 films. Analysis of these spectra to obtain activation energies and pre-exponential factors has been presented elsewhere [19]. A similar dependence on the vanadium oxidation state has also been reported for vanadia films supported on TiO_2(1 1 0) [24,25,33].

Methanol TPD was also used to characterize the reactivity of the high-surface area vanadia/ceria catalyst. As described in the experimental section, these experiments were carried out using a vacuum microbalance system equipped with a mass spectrometer. Methanol and formaldehyde desorption curves obtained during a methanol TPD experiment with a freshly prepared, highly oxidized 8 wt.% vanadia/ceria sample are displayed in Fig. 3. As shown in the figure, CH_3OH desorbed in two overlapping peaks centered at 420 and 470 K, while CH_2O was produced in a single peak centered at 525 K.

The effect of the pretreatment conditions on the CH_2O desorption temperature during a CH_3OH TPD experiment was also studied for the high-surface area vanadia/ceria catalyst. Fig. 4 displays the CH_2O desorption curves obtained for several consecutive CH_3OH TPD experiments with the high-surface area sample. Curve a in the figure corresponds to the freshly prepared sample and is the same as that in Fig. 3. Curve b was obtained in the subsequent CH_3OH TPD experiment. As was also the case for the single crystal

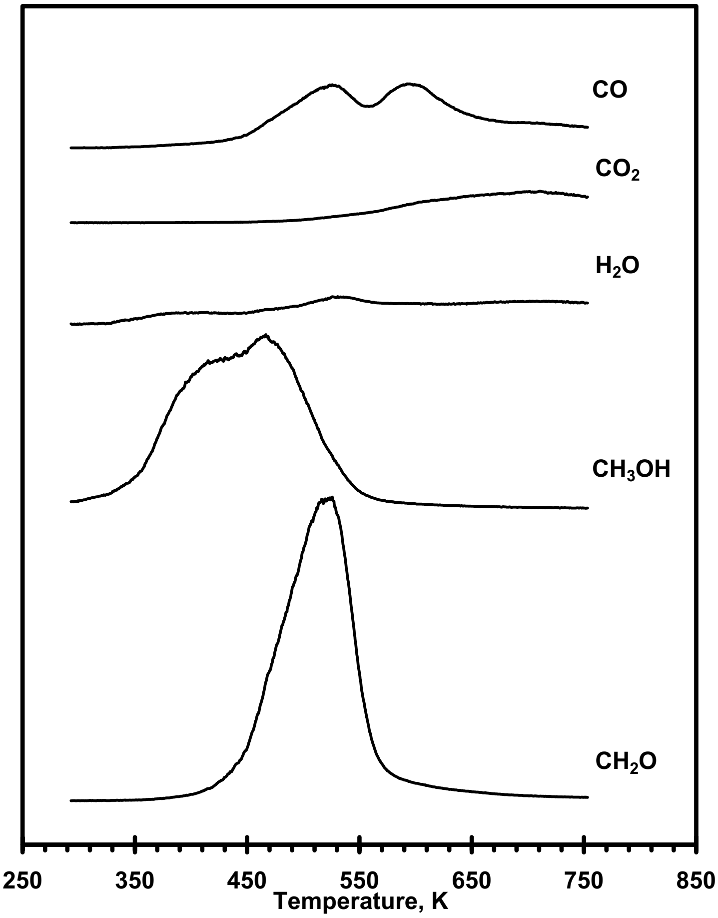

Fig. 3. TPD spectra obtained from a freshly prepared, CH_3OH-dosed, polycrystalline 8 wt.% vanadia/ceria sample.

model catalyst, in the second TPD run, the CH_2O desorption peak shifted to higher temperatures. In this run, the CH_2O desorption curve contains two overlapping peaks centered at 550 and 610 K. The total amount of CH_2O produced was also substantially less in the second run compared to that in the first. In the third CH_3OH TPD run (curve c) only the high-temperature CH_2O peak at 610 K is present. Following the third TPD run the sample was annealed in 1 Torr of O_2 at 750 K. Curve d in Fig. 4 was obtained in a CH_3OH TPD run performed after this oxidation treatment. Note that the CH_2O desorption curve in this run is similar to that obtained from the freshly prepared sample.

Although there are some variations in peak temperatures, which is likely due to differences in heating rates and thermocouple placement, similar trends are observed in the CH_2O desorption curves obtained from the CH_3OH-dosed vanadia/CeO_2(1 1 1) model system and the high-surface area vanadia/ceria catalyst. The monolayer vanadia films in both systems were found to be active for the oxidation of methanol to formaldehyde and the activation energy for dehydrogenation of adsorbed methoxides to produce formaldehyde was found to depend on the sample pretreatment conditions. In light of the UHV TPD and XPS results, the explanation for the peak shifts in the TPD data obtained from the polycrystalline can also be attributed to a change in the oxidation state of the cations in the supported vanadia film. For a fully oxidized sample containing V^{5+}, formaldehyde is produced at 525 K, while on a highly reduced sample containing V^{3+}, formaldehyde is produced at 610 K. The CH_2O peak at 550 K can be attributed to reaction on V^{4+} sites.

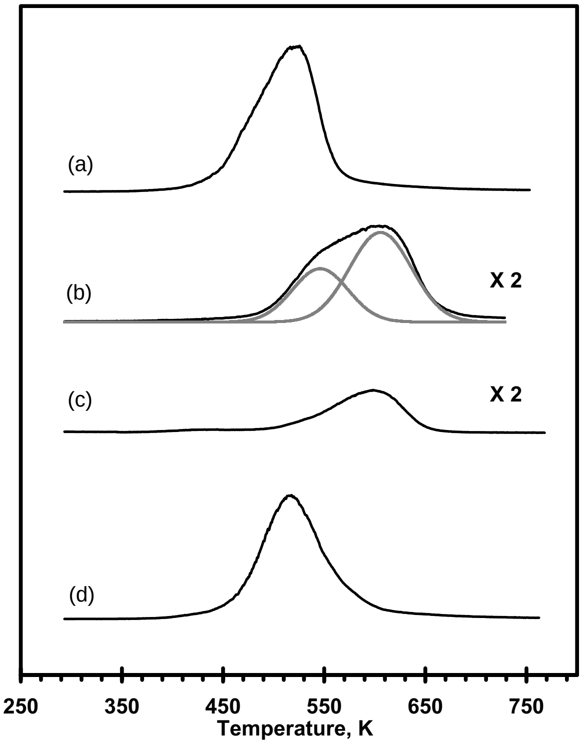

Fig. 4. Formaldehyde desorption spectra obtained from a 8 wt.% vanadia/ceria sample during methanol TPD experiments for various sample pretreatments: (a) freshly prepared sample annealed to 500 K in vacuum prior to the TPD run; (b) subsequent TPD run with the sample used in (a); (c) subsequent TPD run with the sample used in (b); (d) after reoxidation of the sample used in (c) in 1 Torr O_2 at 750 K.

The results of this study, as well as those reported previously for polycrystalline vanadia/titania [34] and vanadia/TiO_2(1 1 0) [20,21,24,25,33], clearly demonstrate that mono and submonolayer vanadia films supported on the surfaces of metal oxide single crystals are excellent model systems of high-surface area supported vanadia catalysts. Although additional studies on a wider range of supports are needed in order to provide insight into the role of the support, the results of the surface science studies of model supported vanadia catalysts that have been carried out to date suggest that this approach holds much promise.

4. Summary

TPD was used to characterize the reactivity of both a model catalyst composed of 0.5 ML vanadia film supported on a CeO_2(1 1 1) single crystal and a high-surface area vanadia/ceria catalyst for the oxidation of methanol to formaldehyde. Both the single crystal and polycrystalline samples were found to be active for this reaction and the temperature at which adsorbed methoxide intermediates underwent dehydrogenation to produce CH_2O during TPD was found to depend on the catalyst pretreatment conditions. XPS results obtained from a vanadia/CeO_2(1 1 1) sample demonstrate that the CH_2O peak temperature during a CH_3OH TPD experiment correlates with the oxidation state of the cations in the supported vanadia layer with reaction on V^{5+} having the lowest activation energy. The similarity in the results obtained in this study from the high and low surface area samples indicates that monolayer vanadia films supported on metal oxide single crystals are excellent models of high-surface area, polycrystalline, supported vanadia catalysts.

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