

# Oxidation of Methanol to Formaldehyde on Vanadia Films Supported on CeO<sub>2</sub>(111)

Gordon S. Wong, Mikael R. Concepcion, and John M. Vohs\*

Department of Chemical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6393

Received: January 17, 2002; In Final Form: April 19, 2002

The reaction of methanol to formaldehyde on both V<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> films supported on CeO<sub>2</sub>(111) was studied by temperature programmed desorption (TPD). Methanol was found to react on monolayer and submonolayer vanadia films to produce formaldehyde, while multilayer films were found to be inactive for this reaction. The kinetics and mechanism of the dehydrogenation of adsorbed methoxides was found to be dependent on the oxidation state of the vanadium cations in the supported vanadia layer. On films that contained V<sup>3+</sup> (i.e., V<sub>2</sub>O<sub>3</sub>), adsorbed methoxy species produced via dissociative adsorption of methanol underwent dehydrogenation to formaldehyde at 600 K. In contrast, on films that contained predominantly V<sup>5+</sup> (i.e., V<sub>2</sub>O<sub>5</sub>), adsorbed methoxy species underwent dehydrogenation to produce formaldehyde at 540 K. Kinetic parameters for the methoxide dehydrogenation to formaldehyde on both V<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> films were determined from the TPD data. The TPD results also provide insight into the thermal stability of supported vanadia films and the role of adsorbed oxygen in the oxidation of methanol to formaldehyde.

## Introduction

Vanadia films supported on a second metal oxide such as TiO<sub>2</sub>, CeO<sub>2</sub>, and ZrO<sub>2</sub> are excellent catalysts for a wide variety of chemical processes including selective oxidation of alcohols, ammoxidation of aromatic hydrocarbons, and the selective catalytic reduction of NO<sub>x</sub> with ammonia (SCR).<sup>1–6</sup> An important aspect of these catalysts is that the active form requires mono- or submonolayer coverages of oxidized vanadium, whereas multilayer coverages are inactive.<sup>1,6–10</sup> The identity of the support also has a significant effect on reactivity. For example, vanadia monolayers supported on TiO<sub>2</sub>, CeO<sub>2</sub>, and ZrO<sub>2</sub> generally exhibit high activity, while those supported on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> exhibit much lower activity.<sup>7,11–13</sup> The origin of this support effect has yet to be fully elucidated. Numerous studies suggest, however, that it is not structural in nature, since the structure of monolayer vanadia films is nearly identical on all of these supports.<sup>3,12</sup>

In an effort to both better understand the influence of the underlying oxide support on reactivity and to determine kinetic parameters for the oxidation of methanol to formaldehyde on supported vanadia, we have been studying model systems consisting of vanadia films grown on single-crystal metal oxide supports. Previously, we have presented results detailing the reactivity of V<sub>2</sub>O<sub>3</sub> films grown on TiO<sub>2</sub>(110).<sup>14,15</sup> Those studies showed that submonolayer and monolayer V<sub>2</sub>O<sub>3</sub> films were active for the oxidation of methanol to formaldehyde, whereas multilayer films were inactive. We have also recently reported on the growth of both V<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> films on CeO<sub>2</sub>(111).<sup>16</sup> In the work reported here we have extended our previous studies on the structure and electronic properties of vanadia films supported on CeO<sub>2</sub>(111) to include temperature programmed desorption (TPD) studies of the reactivity of these films toward methanol.

## Experimental Section

Experiments were conducted in two separate ultrahigh vacuum (UHV) surface analysis chambers. The background

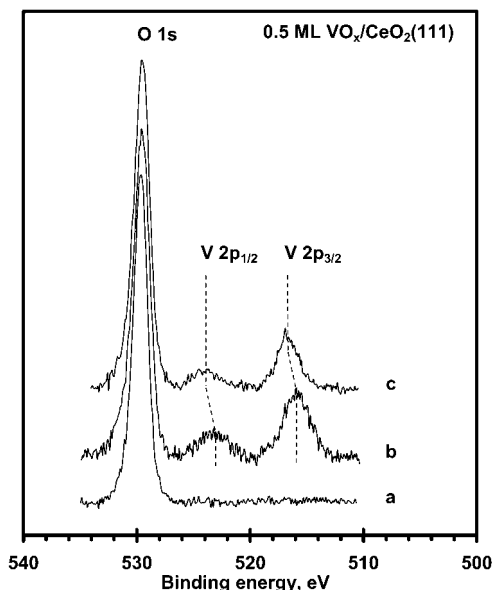
pressure in each chamber was  $\sim 2 \times 10^{-10}$  Torr, and each was equipped with a mass spectrometer (UTI), ion sputter gun (Physical Electronics), quartz crystal film thickness monitor (Maxtek), and vanadium metal deposition source. The UHV chamber used for the TPD experiments was also equipped with a cylindrical mirror electron energy analyzer (Omicron) for Auger electron spectroscopy (AES), while that used for X-ray photoelectron spectroscopy (XPS) contained an X-ray source (VG Microtech) and a hemispherical electron energy analyzer (Leybold-Heraeus).

The CeO<sub>2</sub>(111) single crystal, which was obtained from Commercial Crystal Laboratories, was mounted in a tantalum metal sample holder that 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 CeO<sub>2</sub>(111) sample. Heating was achieved via conduction from the resistively heated tantalum holder. The sample was cleaned using cycles of sputtering with 2 kV Ar<sup>+</sup> ions and annealing at 750 K.

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. The quartz crystal film thickness monitor was used to determine the amount of vanadium deposited. One monolayer of vanadium was defined to be  $1.5 \times 10^{15}$  atoms/cm<sup>2</sup>, which is the density of vanadium atoms on the close packed V(110) surface. The sample was maintained at 300 K during vanadium deposition. To produce a vanadium oxide layer, the sample was annealed in  $10^{-7}$ – $10^{-3}$  Torr of O<sub>2</sub> following vanadium deposition. As will be discussed below, either V<sub>2</sub>O<sub>5</sub> or V<sub>2</sub>O<sub>3</sub> could be produced depending on the O<sub>2</sub> pressure during the oxidation step.

XP spectra were collected using Al K $\alpha$  X-rays. The binding energy scale in the XP spectra was referenced to the primary 3d<sub>5/2</sub> photoemission peak of the Ce<sup>4+</sup> cations in the CeO<sub>2</sub>(111) support, which occurs at 916.96 eV.<sup>17,18</sup> Satellites of the O 1s peak resulting from photoemission excited by Al K $\alpha_3$  and K $\alpha_4$  X-rays fall in the same region of the spectrum as the V 2p peaks. Since these peaks tend to obscure the V 2p peaks, especially

\* Corresponding author. Fax: 1-215-573-2093. E-mail: vohs@seas.upenn.edu.



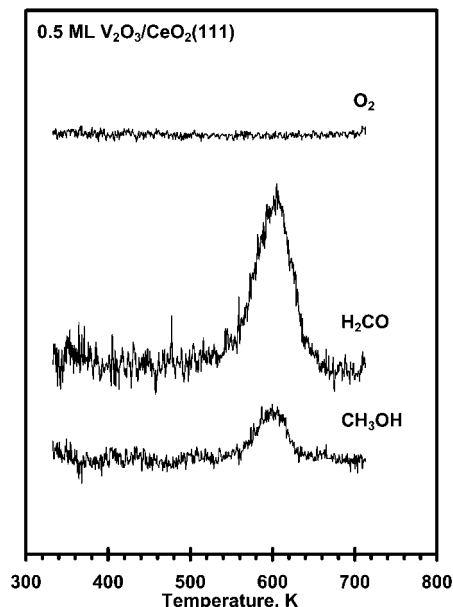
**Figure 1.** V 2p and O 1s XP spectra (a) for clean CeO<sub>2</sub>(111), (b) for a 0.5 monolayer vanadium film on CeO<sub>2</sub>(111) following exposure to 10<sup>-7</sup> Torr of O<sub>2</sub> at 550 K for 1 h, and (c) after exposing the sample in (b) to 10<sup>-3</sup> Torr of O<sub>2</sub> at 400 K for 1 h.

for low vanadium coverages, they were subtracted from the O(1s)/V(2p) spectra presented below using standard techniques.

Methanol (Fisher, HPLC grade) and deuterated methanol (Acros Organics, 99.6%) were purified using repeated freeze-pump-thaw cycles prior to use and were admitted into the vacuum system using a variable leak valve. For TPD experiments, the sample was exposed to 20 langmuir of either methanol or deuterated methanol at 300 K and then heated at a rate of 4.5 K/s. This exposure was found to be sufficient to saturate the surface. Multiple *m/e* values were monitored during each TPD experiment in order to identify the various products. 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.

## Results and Discussion

We have previously reported detailed XPS results for vapor-deposited vanadia films supported on CeO<sub>2</sub>(111).<sup>16</sup> In that study it was shown that the films grow in a layer-by-layer fashion and that for coverages up to one monolayer, either V<sub>2</sub>O<sub>3</sub> or V<sub>2</sub>O<sub>5</sub> films could be produced depending on the growth conditions. This is illustrated in Figure 1 which displays O 1s and V 2p spectra for a 0.5 monolayer vanadia film on CeO<sub>2</sub>(111). Spectrum a in this figure corresponds to clean CeO<sub>2</sub>(111), while spectrum b corresponds to a vanadia film produced by oxidizing a 0.5 monolayer vapor-deposited vanadium film in 10<sup>-7</sup> Torr of O<sub>2</sub> at 550 K for 1 h. The V 2p<sub>3/2</sub> peak in this spectrum is centered at 515.7 eV, which is consistent with the vanadium cations being in the +3 oxidation state (i.e., V<sub>2</sub>O<sub>3</sub>).<sup>19,20</sup> It was found that oxidation treatments that consisted of annealing in less than 10<sup>-7</sup> Torr of O<sub>2</sub> were insufficient to produce films with vanadium cations in higher oxidation states.<sup>16</sup> Films containing V<sup>5+</sup> (i.e., V<sub>2</sub>O<sub>5</sub>) could be produced, however, by annealing in 10<sup>-3</sup> Torr of O<sub>2</sub> at 400 K for 1 h. Spectrum c in Figure 1 was obtained from a 0.5 monolayer vanadia film following this oxidation treatment. Note that the V 2p<sub>3/2</sub> peak has shifted to 516.9 eV, which is consistent with V<sup>5+</sup>.<sup>19</sup> For multilayer vanadia films on CeO<sub>2</sub>(111) it was found that only V<sub>2</sub>O<sub>3</sub> films could be produced by annealing in O<sub>2</sub> at pressures less than 10<sup>-3</sup> Torr.<sup>16</sup>

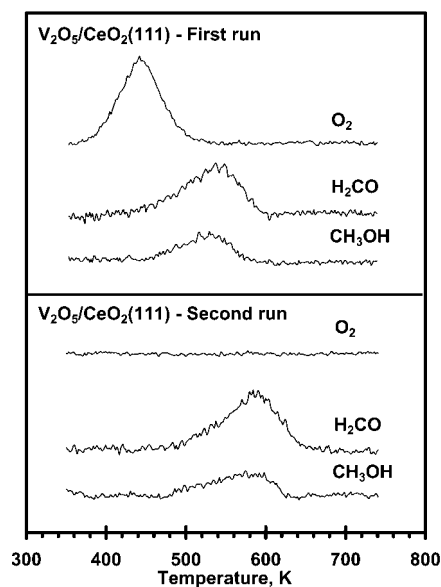


**Figure 2.** CH<sub>3</sub>OH TPD from 0.5 monolayer V<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>(111). Shown here are the O<sub>2</sub>, H<sub>2</sub>CO, and CH<sub>3</sub>OH desorption curves.

TPD spectra obtained from a CH<sub>3</sub>OH-dosed 0.5 monolayer vanadia film supported on CeO<sub>2</sub>(111) are shown in Figure 2. For this sample, the vanadia film was annealed in 10<sup>-7</sup> Torr of O<sub>2</sub> at 550 K for 1 h. As noted above, this procedure produces a film that contains V<sup>3+</sup> cations. The only gaseous products detected during CH<sub>3</sub>OH TPD with this sample were CH<sub>3</sub>OH and CH<sub>2</sub>O, which desorbed at 600 and 605 K, respectively. The ratio of CH<sub>2</sub>O to CH<sub>3</sub>OH produced was roughly 6:1. Since CH<sub>3</sub>OH does not adsorb on stoichiometric CeO<sub>2</sub>(111) at 300 K,<sup>21</sup> these peaks can be assigned to reactions taking place on the vanadia. Neither water nor hydrogen desorption were detected during this TPD experiment. The H<sub>2</sub>O signal did increase slowly, however, at temperatures greater than 400 K. An increasing H<sub>2</sub>O signal with temperature was not observed in blank experiments in which the sample was not dosed with methanol. It is, therefore, likely that reaction of methanol on the surface also resulted in the production of some water.

Methanol TPD results for a more highly oxidized vanadia film supported on CeO<sub>2</sub>(111) are displayed in Figure 3. The data in the upper half of this figure were obtained from a 0.5 monolayer V<sub>2</sub>O<sub>5</sub> film that was produced by annealing the vanadia layer in 10<sup>-3</sup> Torr of O<sub>2</sub> at 400 K for 1 h prior to the TPD experiment. During CH<sub>3</sub>OH TPD with this sample, CH<sub>3</sub>OH and CH<sub>2</sub>O were produced at 530 and 540 K, respectively. The H<sub>2</sub>O signal again increased at temperatures above 400 K, suggesting that some water may also have been produced. Note that the CH<sub>3</sub>OH and CH<sub>2</sub>O peak temperatures are about 70 K less than those obtained from the 0.5 monolayer V<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>(111) sample. The ratio of the areas of the CH<sub>2</sub>O to CH<sub>3</sub>OH peaks was 2:1. In addition to these products, O<sub>2</sub> desorption was also observed during the TPD experiment. Molecular oxygen desorbed in a large peak centered at 450 K. This peak temperature is identical to that reported previously for oxygen desorption from vanadia films pretreated in 10<sup>-3</sup> Torr of O<sub>2</sub>.<sup>16</sup> XPS studies show that desorption of O<sub>2</sub> at 450 K does not result in the reduction of the vanadia layer. Thus, this peak is most likely due to desorption of molecularly adsorbed oxygen.

The lower half of Figure 3 displays the results of a CH<sub>3</sub>OH TPD run that was performed immediately following the run shown in the upper half of the figure. Oxygen desorption did



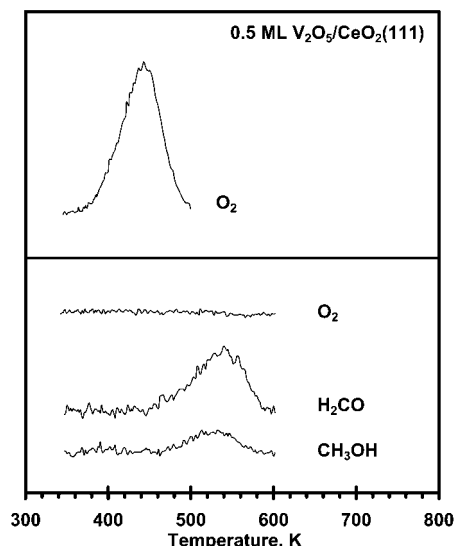
**Figure 3.**  $\text{O}_2$ ,  $\text{H}_2\text{CO}$ , and  $\text{CH}_3\text{OH}$  desorption spectra obtained from a  $\text{CH}_3\text{OH}$ -dosed 0.5 monolayer  $\text{V}_2\text{O}_5$  film on  $\text{CeO}_2(111)$ . The top panel displays spectra from the first run of a freshly oxidized sample, while the bottom panel displays spectra obtained in the subsequent run.

not occur in this TPD run. Methanol and formaldehyde peaks are centered at 590 and 595 K, respectively, and both contain broad leading edges, suggesting that the peaks are composed of overlapping features. Note that except for the broad leading edges, this set of TPD results is similar to that in Figure 2 for 0.5 monolayer  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$ . This indicates that the  $\text{V}_2\text{O}_5$  film underwent reduction during the first TPD run and that the predominant oxidation state of the vanadium cations in the film was +3. These results demonstrate that the temperature at which formaldehyde is produced during methanol TPD on supported vanadia films can be used as a chemical probe for the oxidation state of the vanadium cations.

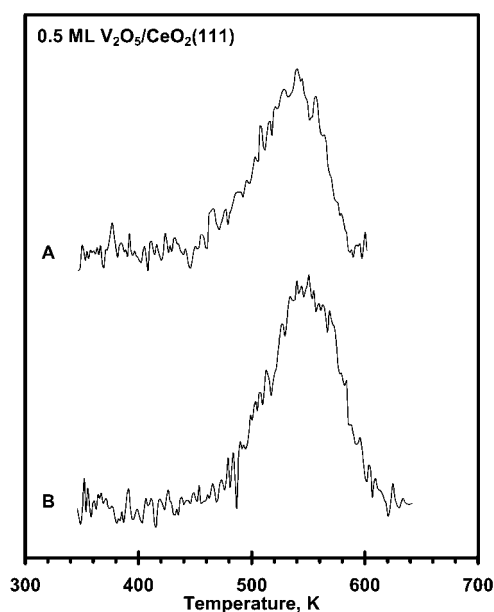
Although the data in Figure 3 demonstrate the influence of the oxidation state of the vanadium cations on reactivity toward methanol, they also raise several questions. For example it is not clear whether the adsorbed oxygen species plays a role in the oxidation of the adsorbed methoxides in the case of the  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$  sample. It is also not clear if the reduction of the  $\text{V}_2\text{O}_5$  film to  $\text{V}_2\text{O}_3$  that occurred during the first TPD run was a result of the reaction of methanol on the surface, heating the sample to 750 K, or a combination of the two.

To assess the influence of the  $\text{O}_2$  species on the reactivity of the supported  $\text{V}_2\text{O}_5$  film, the following series of experiments were performed. A 0.5 monolayer  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$  sample was prepared by oxidizing in  $10^{-3}$  Torr of  $\text{O}_2$ . The sample was then flashed to 500 K in order to desorb the  $\text{O}_2$  species. The  $\text{O}_2$  desorption curve obtained while flashing is displayed in the upper portion of Figure 4. The sample was then dosed with  $\text{CH}_3\text{OH}$  at room temperature and a TPD experiment was performed. Methanol, formaldehyde, and oxygen desorption curves obtained in this TPD run are displayed in the lower portion of Figure 4. Note that in this TPD experiment, even though  $\text{O}_2$  desorption at 450 K was not detected, formaldehyde was still produced at 540 K. This is the same temperature as that for samples in which the oxygen species was present on the surface. This result demonstrates that the adsorbed oxygen species does not play a role in the oxidation of methoxides to formaldehyde on the  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$  model catalyst.

As described earlier, a  $\text{CH}_3\text{OH}$  TPD experiment in which the sample is heated to 750 K results in reduction of supported

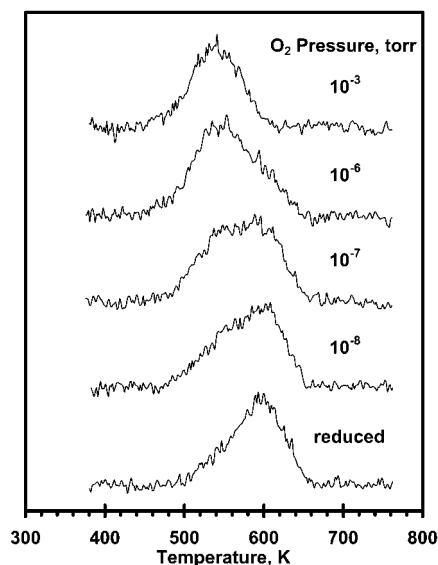


**Figure 4.** (Upper panel)  $\text{O}_2$  desorption curve from a freshly prepared 0.5 monolayer  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$  sample. The temperature ramp in this run was stopped at 500 K. Immediately after this run, the sample was dosed with  $\text{CH}_3\text{OH}$  and a TPD run was performed. The desorption curves from this second run are shown in the lower panel.



**Figure 5.**  $\text{H}_2\text{CO}$  desorption curves from two consecutive  $\text{CH}_3\text{OH}$  TPD runs with a 0.5 monolayer  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$  sample. The temperature ramp was stopped at 600 K in the first run (spectrum A) and 640 K in the second run (spectrum B).

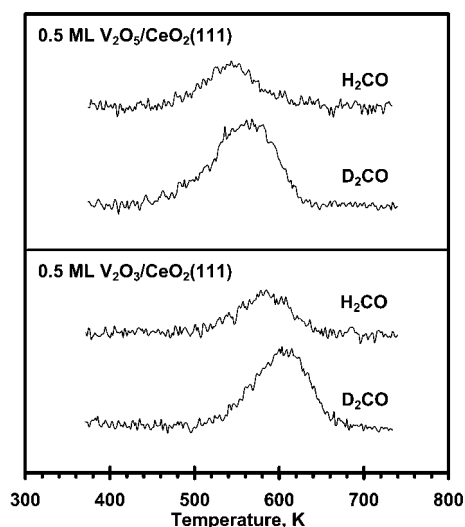
$\text{V}_2\text{O}_5$  to  $\text{V}_2\text{O}_3$  (see Figure 3) and a shift in the temperature at which  $\text{CH}_2\text{O}$  is produced from 540 to 595 K. To provide additional insight into the effect of annealing temperature on reactivity and the extent of reduction of the vanadia layer, a  $\text{CH}_3\text{OH}$  TPD experiment was performed using a freshly prepared  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$  sample in which the temperature ramp was stopped at 600 K and then a second  $\text{CH}_3\text{OH}$  TPD run was performed. The  $\text{CH}_2\text{O}$  desorption curve from the first run in this set of experiments is displayed at the top of Figure 5 and contains a  $\text{CH}_2\text{O}$  peak centered at 540 K, as would be expected for a fully oxidized vanadia film. As shown in the lower panel of the figure, the  $\text{CH}_2\text{O}$  peak in the spectrum from the second run is shifted slightly upward to 550 K. Although this shift suggests some reduction of the vanadia layer occurred during the first TPD run, the magnitude of the shift is significantly



**Figure 6.**  $\text{H}_2\text{CO}$  desorption curves from  $\text{CH}_3\text{OH}$ -dosed 0.5 monolayer  $\text{VO}_x/\text{CeO}_2(111)$ . In this set of experiments a reduced  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$  sample was dosed with  $\text{O}_2$  and then a  $\text{CH}_3\text{OH}$  TPD run was performed. The oxygen dose consisted of exposing the sample to the  $P_{\text{O}_2}$  specified in the figure for 30 s.

less than that obtained following a TPD run in which the sample was heated to 750 K (see Figure 3). These results, therefore, demonstrate that in the runs in which the sample was heated to 750 K, reduction of the vanadia layer is primarily thermally induced and not due to reaction of methanol on the surface. This conclusion is consistent with our previous XPS results, which also show that reduction of the supported  $\text{V}_2\text{O}_5$  layer occurs upon heating to temperatures in excess of 650 K.<sup>16</sup>

As noted above, production of a  $\text{V}_2\text{O}_5$  film on  $\text{CeO}_2(111)$  required oxidation of a vapor-deposited vanadium layer in  $10^{-3}$  Torr of  $\text{O}_2$  at 400 K. Annealing in lower pressures of oxygen produced films that contained only  $\text{V}^{3+}$  (i.e.,  $\text{V}_2\text{O}_3$ ). It was observed, however, that  $\text{V}_2\text{O}_3$  layers that were produced by heating a  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$  sample to 750 K could be at least partially reoxidized using less stringent conditions. This is illustrated in Figure 6, which displays the  $\text{CH}_2\text{O}$  desorption curves obtained for  $\text{CH}_3\text{OH}$  TPD runs with  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$  samples that had been reduced by a previous  $\text{CH}_3\text{OH}$  TPD run and then reoxidized. The reoxidation treatments consisted of exposing the reduced sample to  $10^{-8}$ ,  $10^{-7}$ ,  $10^{-6}$ , and  $10^{-3}$  Torr of  $\text{O}_2$  for 30 s. For comparison, the  $\text{CH}_2\text{O}$  TPD curve obtained from a reduced sample, prior to reoxidation, is also included in the figure. The data in this figure show that even small doses of  $\text{O}_2$  are sufficient to partially reoxidize the vanadia layer. For example, the  $\text{CH}_2\text{O}$  spectrum obtained following exposure of a reduced sample to  $10^{-8}$  Torr of  $\text{O}_2$  for 30 s (0.3 langmuir) can be resolved into two overlapping peaks centered at 540 and 600 K. These peaks can be assigned to reactions taking place on  $\text{V}^{5+}$  and  $\text{V}^{3+}$ , respectively. The ratio of the area of the low-temperature peak to that at high temperature in this run was approximately 1:2. This ratio increased with increasing oxygen exposure in the reoxidation step. An  $\text{O}_2$  exposure of  $10^{-3}$  Torr of  $\text{O}_2$  for 30 s was sufficient to completely reoxidize the vanadia film and only the low-temperature  $\text{CH}_2\text{O}$  peak, indicative of reaction on  $\text{V}^{5+}$ , was observed in the spectrum from this sample. These results suggest that after a  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$  sample has initially been synthesized, it is relatively easy to cycle the oxidation state of the vanadium cations between +5 and +3. One possible explanation for this observation is that a structural rearrangement of the vanadia layer must take place during the



**Figure 7.**  $\text{H}_2\text{CO}$  and  $\text{D}_2\text{CO}$  desorption spectra from 0.5 monolayer vanadia film supported on  $\text{CeO}_2(111)$ , when dosed with  $\text{CH}_3\text{OH}$  or  $\text{CD}_3\text{OD}$ , respectively. The data in the top panel were obtained from a  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$  sample, while data in the bottom panel were obtained from a  $\text{V}_2\text{O}_3/\text{CeO}_2(111)$  sample.

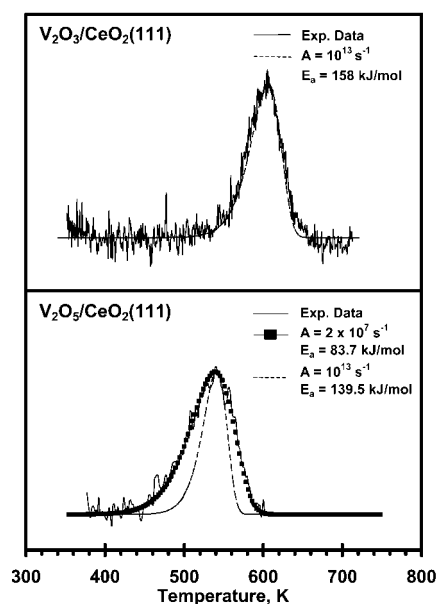
first oxidation treatment in order to form  $\text{V}_2\text{O}_5$  and this makes it more difficult to initially synthesize the fully oxidized film.

The influence of the vanadia coverage on the reactivity of  $\text{VO}_x/\text{CeO}_2(111)$  was also investigated. For vanadia coverages up to 1 monolayer the TPD results for both  $\text{V}_2\text{O}_5$  and  $\text{V}_2\text{O}_3$  films were similar to those reported above for a 0.5 monolayer film. The only difference being the intensity of the high-temperature  $\text{CH}_2\text{O}$  and  $\text{CH}_3\text{OH}$  desorption peaks. The intensity of these peaks increased with vanadia coverage for coverages up to 0.5 monolayer and then slowly decreased with further increases in vanadia coverage. Multilayer  $\text{V}_2\text{O}_3$  films on  $\text{CeO}_2(111)$  were found to be unreactive and methanol adsorbed only molecularly on these films. As noted above, it was not possible to produce multilayer  $\text{V}_2\text{O}_5$  films on  $\text{CeO}_2(111)$ .

To provide additional insight into the mechanism of the reaction that produces  $\text{CH}_2\text{O}$  at 540 K on the  $\text{V}_2\text{O}_5$  films and 600 K on the  $\text{V}_2\text{O}_3$  films, TPD experiments were conducted in which  $\text{CD}_3\text{OD}$  was used as the reactant. Figure 7 presents a comparison of the formaldehyde desorption curves obtained when using  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OD}$  as the reactants for 0.5 monolayer  $\text{V}_2\text{O}_5$  (upper panel) and  $\text{V}_2\text{O}_3$  (lower panel) films. Note that a kinetic isotope effect is observed for both the oxidized and partially reduced samples. For  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$ ,  $\text{CH}_2\text{O}$  is produced at 540 K, while  $\text{CD}_2\text{O}$  is produced at 560 K. For the  $\text{V}_2\text{O}_3/\text{CeO}_2(111)$  sample, the peak temperature for  $\text{CD}_2\text{O}$ , 610 K, is again 20 K higher than that for  $\text{CH}_2\text{O}$ , which was at 590 K. These results demonstrate that C–H bond cleavage is the rate-limiting step in the formation of  $\text{CH}_2\text{O}$  from adsorbed methoxide intermediates on both  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$  and  $\text{V}_2\text{O}_3/\text{CeO}_2(111)$ .

Kinetic parameters for the rate-limiting step in the formation of  $\text{CH}_2\text{O}$  from adsorbed methoxide species on both the  $\text{V}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  films were deduced from the TPD results. This was done by simulating TPD curves and adjusting the preexponential factor and activation energy in order to obtain the best fit to the experimental data. These simulation results along with the experimental data are presented in Figure 8. The upper panel in this figure presents the TPD simulation results for  $\text{CH}_2\text{O}$  desorption from a 0.5 monolayer  $\text{V}_2\text{O}_3$  film supported on  $\text{CeO}_2(111)$ . Note that the simulated TPD curve obtained using a preexponential factor of  $10^{13} \text{ s}^{-1}$  and an activation energy of





**Figure 8.**  $\text{H}_2\text{CO}$  desorption spectra from  $\text{CH}_3\text{OH}$ -dosed 0.5 monolayer  $\text{V}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  films on  $\text{CeO}_2(111)$ . Curve fits used to determine the kinetic parameters for the  $\text{H}_2\text{CO}$  desorption peaks are also displayed in the figure.

158 kJ/mol provides an excellent fit to the data. On the basis of transition state theory, the magnitude of the preexponential factor depends on the entropy of activation ( $\Delta S^\ddagger$ ). A  $\Delta S^\ddagger$  value of zero produces a preexponential factor that is approximately  $10^{13} \text{ s}^{-1}$ . Thus, these results indicate that  $\Delta S^\ddagger$  for the dehydrogenation of a surface methoxide to produce formaldehyde on  $\text{V}_2\text{O}_3/\text{CeO}_2(111)$  is very small. This in turn suggests that the transition state for this reaction resembles the reactant (i.e., there is an early transition state).

In addition to being at a lower temperature, the  $\text{CH}_2\text{O}$  desorption peak from a 0.5 monolayer  $\text{V}_2\text{O}_5$  film on  $\text{CeO}_2(111)$  is much broader than that from  $\text{V}_2\text{O}_3/\text{CeO}_2(111)$ . As shown in the lower panel of Figure 8, the  $\text{CH}_2\text{O}$  peak from  $\text{V}_2\text{O}_5/\text{CeO}_2(111)$  cannot be adequately fit using a preexponential factor of  $10^{13} \text{ s}^{-1}$ . The simulated TPD curve obtained using a preexponential factor of  $10^{13} \text{ s}^{-1}$  and an activation energy of 139.5 kJ/mol gives the correct peak temperature but produces a peak that is much narrower than that in the experimental data. A much lower value for the preexponential factor is needed in order to obtain a good fit to the data. As shown in the figure, a simulated TPD curve obtained using a preexponential factor of  $2 \times 10^7 \text{ s}^{-1}$  and an activation energy of 83.7 kJ/mol provides an excellent fit to the data. Since these values for the preexponential factor and activation energy were determined by fitting to a rather limited data set (i.e., one TPD run), one needs to be cautious in interpreting this result. Other factors such as defects and a distribution of vanadium oxidation states in the film (e.g., a mixture of  $\text{V}^{5+}$  and  $\text{V}^{4+}$ ) might also produce broad peaks. The fact that the calculated activation energy, 83.7 kJ/mol, is nearly identical to the reported value of the apparent activation energy for this reaction determined from steady-state kinetics data using a high surface area vanadia/ceria catalyst,<sup>11,12</sup> however, provides some additional credence to the kinetic parameters determined from the TPD data.

Finally, it is interesting to compare the results obtained in the present study to those reported previously for the reaction of methanol on monolayer films of  $\text{V}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  supported on  $\text{TiO}_2(110)$ . Wang et al. have performed  $\text{CH}_3\text{OH}$  TPD on a 1 monolayer  $\text{V}_2\text{O}_5/\text{TiO}_2(110)$  sample and found that  $\text{CH}_2\text{O}$  was

produced at 517 K.<sup>22</sup> We have previously shown that during TPD, methanol also reacts on mono- and submonolayer  $\text{V}_2\text{O}_3$  films supported on  $\text{TiO}_2(110)$  to produce  $\text{CH}_2\text{O}$  between 600 and 700 K.<sup>14,15</sup> In this case, the  $\text{CH}_2\text{O}$  desorption temperature was found to be dependent on the vanadia coverage, with lower coverages giving slightly higher temperatures. Note that these results are similar to those reported here for  $\text{VO}_x/\text{CeO}_2(111)$  and also demonstrate that the activation energy for dehydrogenation of methoxides to formaldehyde is lower on supported  $\text{V}_2\text{O}_5$  relative to that on supported  $\text{V}_2\text{O}_3$ .

## Conclusions

The results of this study demonstrate that submonolayer and monolayer coverages of vanadia supported on  $\text{CeO}_2(111)$  are active for the oxidation of methanol to formaldehyde. The mechanism of this reaction, however, was found to be dependent on the oxidation state of the vanadium cations in the supported vanadia film. Methanol adsorbs dissociatively on monolayer and submonolayer  $\text{V}_2\text{O}_3$  films on  $\text{CeO}_2(111)$  and the resulting surface methoxides undergo dehydrogenation near 600 K to produce formaldehyde. Analysis of the TPD data indicates that the preexponential factor and activation energy for this reaction are  $10^{13} \text{ s}^{-1}$  and 158 kJ/mol, respectively. In contrast to supported  $\text{V}_2\text{O}_3$ , adsorbed methoxide intermediates produced via dissociative adsorption of methanol on submonolayer and monolayer  $\text{V}_2\text{O}_5$  films on  $\text{CeO}_2(111)$ , undergo dehydrogenation to produce formaldehyde at 540 K. The preexponential factor and activation energy for this reaction on supported  $\text{V}_2\text{O}_5$  were found to be  $2 \times 10^7 \text{ s}^{-1}$  and 83.7 kJ/mol, respectively.

**Acknowledgment.** We gratefully acknowledge the financial support of the National Science Foundation (Grant No. CTS-9712774) and the Laboratory for Research on the Structure of Matter at the University of Pennsylvania for the use of its facilities.

## References and Notes

- (1) Bond, G. C.; Tahir, S. F. *Appl. Catal. A* **1991**, 71, 1.
- (2) Bond, G. C. *Appl. Catal. A* **1997**, 157, 91.
- (3) Wachs, I. E.; Weckhuysen, B. M. *Appl. Catal. A* **1997**, 157, 67.
- (4) Centi, G. *Appl. Catal. A* **1996**, 147, 267.
- (5) Blasco, T.; Lopez Nieto, J. M. *Appl. Catal. A* **1997**, 157, 117.
- (6) Forzatti, P.; Tronconi, E.; Elmi, A. S.; Busca, G. *Appl. Catal. A* **1997**, 157, 387.
- (7) Deo, G.; Wachs, I. E. *J. Catal.* **1991**, 129, 307.
- (8) Khodakov, A.; Olthof, B.; Bell, A. T.; Iglesia, E. *J. Catal.* **1999**, 181, 205.
- (9) Went, G. T.; Leu, L.; Rosin, R. R.; Bell, A. T. *J. Catal.* **1992**, 134, 492.
- (10) Roozeboom, F.; Cordingley, P. D.; Gellings, P. J. *J. Catal.* **1981**, 68, 464.
- (11) Burcham, L. J.; Wachs, I. E. *Catal. Today* **1999**, 49, 467.
- (12) Wachs, I. E.; Deo, G.; Juskalis, M. V.; Weckhuysen, B. M. *Stud. Surf. Sci. Catal.* **1997**, 109, 305.
- (13) Deo, G.; Wachs, I. E. *J. Catal.* **1994**, 146, 323.
- (14) Wong, G. S.; Kragten, D. D.; Vohs, J. M. *Surf. Sci.* **2000**, 452, L293.
- (15) Wong, G. S.; Kragten, D. D.; Vohs, J. M. *J. Phys. Chem. B* **2001**, 105, 1366.
- (16) Wong, G. S.; Vohs, J. M. *Surf. Sci.* **2002**, 498, 266.
- (17) Pfau, A.; Schierbaum, K. D. *Surf. Sci.* **1994**, 321, 71.
- (18) Pfau, A.; Schierbaum, K. D.; Gopel, W. *Surf. Sci. Spectra* **1998**, 4, 288.
- (19) Sawatsky, G. A.; Post, D. *Phys. Rev. B* **1979**, 20, 1546.
- (20) Demeter, M.; Neumann, M.; Reichelt, W. *Surf. Sci.* **2000**, 454–456, 41.
- (21) Ferrizz, R. M.; Wong, G. S.; Egami, T.; Vohs, J. M. *Langmuir* **2001**, 17, 2464.
- (22) Wang, Q.; Madix, R. J. *Surf. Sci.* **2001**, 474, L213.