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A TPD study of the partial oxidation of methanol to formaldehyde on CeO_2-supported vanadium oxide

T. Feng and J.M. Vohs *

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

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Abstract

The partial oxidation of methanol to formaldehyde on ceria-supported monolayer vanadium oxide was studied using temperature-programmed desorption (TPD), microcalorimetry, and X-ray photoelectron spectroscopy (XPS). Methanol TPD demonstrated that the activation energy for the dehydrogenation of adsorbed methoxides to produce formaldehyde is a function of the oxidation state of the vanadium cations in the supported layer. During CH_3OH TPD, CH_2O was produced at 525, 550, and 610 K, on V^{5+}, V^{4+}, and V^{3+}, respectively. The heat of reoxidation of supported vanadia/ceria samples that had been reduced by performing a CH_3OH TPD experiment was measured using microcalorimetry and found to be 245 kJ/mol of O_2. The heat of adsorption of CH_3OH on the vanadia layer was also measured and found to be 80 kJ/mol on both oxidized and partially reduced VO_x/CeO_2 samples. The implications of these results for understanding the mechanism of methanol oxidation on supported vanadia are discussed.

1. Introduction

Supported vanadia catalysts exhibit high activity and selectivity for a variety of reactions including the oxidation of *o*-xylene to phthalic anhydride, methanol to formaldehyde, and the selective catalytic reduction of NO_x with ammonia (SCR) [1–3]. An important aspect of these catalysts is that the vanadia only exhibits high activity when present as a monolayer or submonolayer species. While it is well established that the structure of the surface vanadia complex is not a strong function of the identity of the underlying oxide support [4–7], the overall reactivity of supported vanadia catalysts is still highly support dependent. For example, the turnover frequency for the selective oxidation of methanol to formaldehyde at 525 K varies from 3.53 s^{-1} for V_2O_5/ZrO_2 to 1.01 s^{-1} for V_2O_5/TiO_2 to 0.057 s^{-1} for V_2O_5/Al_2O_3 [8]. The origin of the influence of the support on reactivity is still not well understood, but it is generally thought that the V–O–support bonds play an important role in determining reactivity [9,10].

Another interesting aspect of supported vanadia catalysts is that despite the fact that the overall reactivity depends on the identity of the support [2,6], the apparent activation energy for selective oxidation reactions, such as the oxidation of methanol to formaldehyde, is largely support independent. The apparent activation energy for this reaction has been reported to be approximately 84 kJ/mol for a wide range of supports (e.g., TiO_2, Nb_2O_5, ZrO_2, CeO_2, Al_2O_3, and SiO_2) [9,11,12]. Based in large part on this observation it has been suggested that the support must influence other parameters such as the heat of dissociative adsorption of methanol. Unfortunately, in kinetics studies employing flow reactors it is generally not possible to independently determine all the parameters that appear in the overall kinetics expression. Thus, important kinetics parameters such as the activation energy for the dehydrogenation of adsorbed methoxide intermediates, which is likely to be the rate-determining step, have in most cases not been directly measured. Understanding how the underlying support influences the kinetics parameters for the individual elementary steps may be key to unraveling the origins of the support effect.

In order to provide a more detailed description of reaction mechanisms, structure-activity relationships, and the origin of the support effect in supported vanadia catalysts our research group over the past several years has been studying this catalytic system using a combination of temperature-programmed desorption (TPD), thermal gravimetric analysis (TGA), microcalorimetry, and X-ray photoelectron spec-

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* Corresponding author.
E-mail address: vohs@seas.upenn.edu (J.M. Vohs).

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troscopy (XPS). This work has made use of both model systems consisting of vapor-deposited vanadia films supported on metal oxide single crystals [13–17] and high surface area supported vanadia catalysts [18,19]. One of the specific goals of these studies has been to measure kinetics parameters for the individual elementary steps in the oxidation of methanol to formaldehyde (e.g., dissociative adsorption of methanol, and dehydrogenation of surface methoxides) as a function of the identity of the support. In this paper we have extended our previous studies to include the adsorption and reaction of methanol on polycrystalline VO_x/CeO_2.

2. Experimental

2.1. Catalyst preparation

The cerium oxide used as the support in this study was synthesized by annealing $Ce(NO_3)_3 \cdot 6H_2O$ (99.5%, Alfa Aesar) in air at 875 K for 5 h. The surface area of the resulting ceria as measured using the BET method was 35 m^2/g. Vanadia was deposited on the ceria support using incipient wetness of an aqueous solution of ammonium metavanadate (NH_4VO_3, Sigma) and oxalic acid ($C_2O_4H_2$, Aldrich) in a 1:2 molar ratio. The concentration of vanadate and the amount of impregnation solution was adjusted in order to produce catalysts with vanadia weight loadings between 1 and 10 wt%. After impregnation of the vanadate the samples were dried overnight at 400 K and then calcined in air at 775 K for 5 h.

2.2. Temperature-programmed desorption

The TPD apparatus used in this study has previously been described in detail [19] and consisted of a Cahn vacuum microbalance that was modified to allow the sample to be heated using an external oven. The system was also equipped with a diffusion pump and a mass spectrometer (Thermo ONIX). For TPD studies 30–40 mg of catalyst was loaded into the sample pan of the microbalance and the system was evacuated to a baseline pressure of 10^{-7} Torr. In most cases after being placed into the TPD system the vanadia/ceria sample was pretreated by heating in vacuum to 475 K in order to remove adsorbed water, surface hydroxyls, and other weakly adsorbed impurities. This annealing temperature was chosen based on results obtained in a previous study of vanadia/$CeO_2(111)$ [15] which showed that it is sufficiently low to not induce reduction of the vanadia layer. For a TPD experiment the catalyst was initially exposed to ~ 15 Torr methanol vapor at room temperature. The exposure time varied somewhat from run to run but was always long enough to ensure that the sample was saturated with methanol as determined by a leveling off of the weight gain. After pumping the system back to its base pressure and allowing the sample weight to again stabilize, the sample was heated to 800 K at a rate of 15 K/min. While heating, the desorbing species were monitored using the mass spectrometer. Multiple m/e ratios were collected during each TPD run. Individual products were identified by their characteristic mass fragmentation patterns. The desorption spectra for specific molecules presented below have been corrected for overlapping cracking fragments from other products and quantified using standard procedures.

2.3. Calorimetry

Calorimetry was used to determine the heats of reoxidation of partially reduced catalysts and the heats of adsorption of CH_3OH on fully oxidized and partially reduced catalysts. A detailed description of the custom-built calorimeter used in this study can be found in a previous publication [18,20]. Approximately 2 g of the catalyst was used in each calorimetry experiment. The sample was initially heated to 475 K in vacuum ($\sim 10^{-3}$ Torr) to remove adsorbed water. In order to partially reduce the supported vanadia layer the samples were exposed to 50 Torr of CH_3OH for 10 to 15 min, the system was then evacuated, and the sample was heated to 750 K at a rate of 15 K/min (this procedure was designed to simulate the conditions used in the TPD experiments). In one set of experiments with a pure ceria sample, the sample was reduced by continuous exposure to 10 Torr of H_2 at 775 K. The heats of adsorption of oxygen on the reduced samples and methanol on both fully oxidized and reduced samples were measured for a series of small pulses of each gas with the sample held at 425 and 295 K, respectively.

2.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectra of the supported vanadium oxide catalysts were collected using an ultrahigh vacuum chamber equipped with an X-ray source (VG Microtech) and a hemispherical electron energy analyzer (Leybold-Heraeus). Samples analyzed by XPS consisted of self-supporting disks that were produced by pressing ~ 200 mg of the powder catalyst. The UHV analysis chamber was equipped with a sample transfer system and a prechamber in which a sample could be annealed in a controlled gas ambient. XP spectra were collected using Al-K_α X-rays. The binding energy scale was referenced to the primary O 1s photoemission peak located at 529.6 eV. Satellites of this peak resulting from photoemission excited by Al-K_{α_3} and K_{α_4} X-rays which fall in the same region of the spectrum as V 2p peaks were subtracted using standard procedures.

3. Results

3.1. CH_3OH TPD—CeO_2

To provide a basis for comparison, the reaction of methanol on the bare ceria support was initially characterized using TPD. The ceria sample used in these experiments

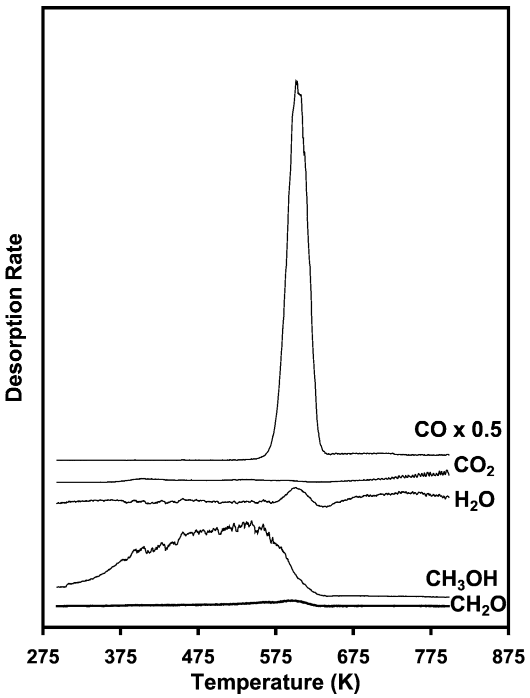


Fig. 1. TPD spectra obtained from CH_3OH-dosed CeO_2.

was pretreated by annealing in vacuum at 475 K. TPD spectra obtained from methanol-dosed CeO_2 are displayed in Fig. 1. The primary desorbing species were methanol, which desorbed in a broad feature spanning from 350 to 630 K, and CO which desorbed in a large, narrow peak centered at 605 K. The only other products detected were small amounts of CH_2O and H_2O, which were produced at 595 and 605 K, respectively. Previous TPD studies of the oxidation of methanol on ceria single crystals and ceria thin films have shown that this reaction is structure sensitive [21,22] with the peak temperatures and product distributions being a function of the extent of reduction of the ceria surface. Nearly stoichiometric CeO_2 surfaces are relatively inactive [21] while partially reduced surfaces are active for the oxidation of CH_3OH to CH_2O and CO with the selectivity to CO increasing with the extent of reduction of the ceria surface. Thus, the fact that CO was the primary oxidation product in the CH_3OH TPD experiments with the polycrystalline ceria sample indicates that the surface of this sample contained a high concentration of oxygen vacancies. As will be shown below, the CO peak at 605 K during TPD with a CH_3OH-dosed sample can be used as a signature for the reaction of CH_3OH on this surface.

3.2. CH_3OH TPD—vanadia/ceria

CH_3OH TPD data were collected for a series of vanadia/ceria catalysts. The specific vanadia loadings that were included in the series were 1, 3, 4, 5, 6, 8, and 10 wt%. In this series of experiments the catalyst sample was initially outgassed in the vacuum system for several hours at 300 K and then briefly annealed at 475 K in order to remove adsorbed water. After the sample had cooled to room temperature a methanol TPD experiment was performed. The only products in the TPD spectra for the vanadia/ceria catalysts were CH_3OH, CH_2O, CO, H_2O, and CO_2. Complete sets of TPD data for the 1 and 6 wt% samples are displayed in Fig. 2. Relative product yields (excluding methanol) for the TPD runs for all vanadia coverages are listed in Table 1. As shown in Fig. 2, the CH_3OH desorption curves varied somewhat with vanadia coverage and contained broad features between 350 and 600 K. For all vanadia coverages the primary oxidation products were CO and CH_2O. Only small amounts of CO_2 and H_2O were produced. The H_2CO to CO ratio was a function of the vanadia coverage and increased from 0.35 for the 1 wt% V_2O_5 to 3.0 for 6 wt% V_2O_5.

The trends in the desorption spectra for the oxidation products with vanadia coverage can be seen more clearly in Figs. 3 and 4, which display the CO and CH_2O desorption spectra, respectively, for all of the vanadia coverages that

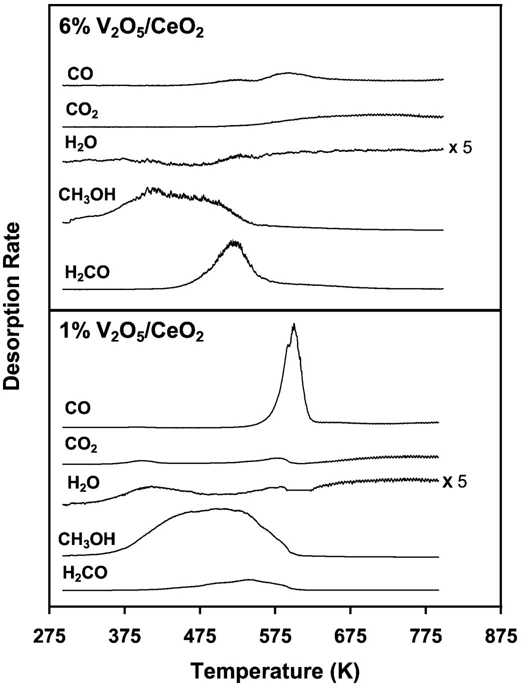


Fig. 2. TPD spectra obtained from CH_3OH-dosed 1 and 6 wt% V_2O_5 supported on ceria.

Table 1
Relative product yields (excluding CH_3OH)

Sample	Relative yield (%)			
	CO	H_2CO	H_2O	CO_2
CeO_2	93	5	2	0
1 wt% V_2O_5/CeO_2	62.3	22.0	6.2	9.6
3 wt% V_2O_5/CeO_2	40.9	46.7	7.1	5.3
4 wt% V_2O_5/CeO_2	23.6	59.7	10.9	5.8
5 wt% V_2O_5/CeO_2	19.5	66.4	2.5	6.4
6 wt% V_2O_5/CeO_2	18.8	56.7	19.1	5.4
8 wt% V_2O_5/CeO_2	23.3	57.8	10.7	8.2
10 wt% V_2O_5/CeO_2	13.9	49.5	22.1	14.5

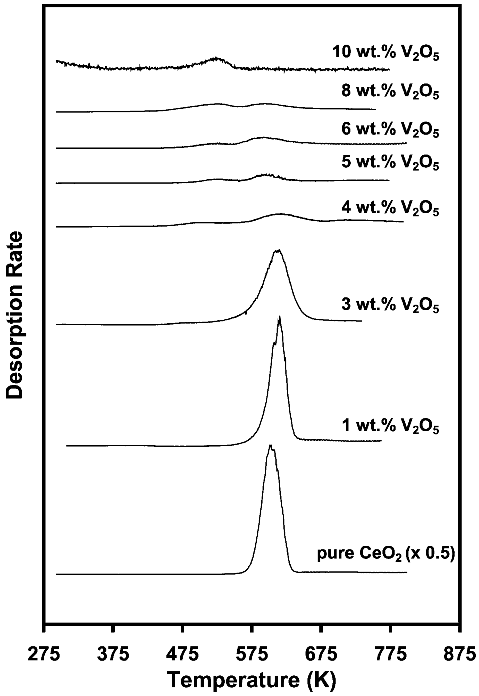


Fig. 3. CO desorption spectra obtained during TPD with CH_3OH-dosed samples as a function of the vanadia weight loading. The spectra have been normalized to take into account variations in sample mass.

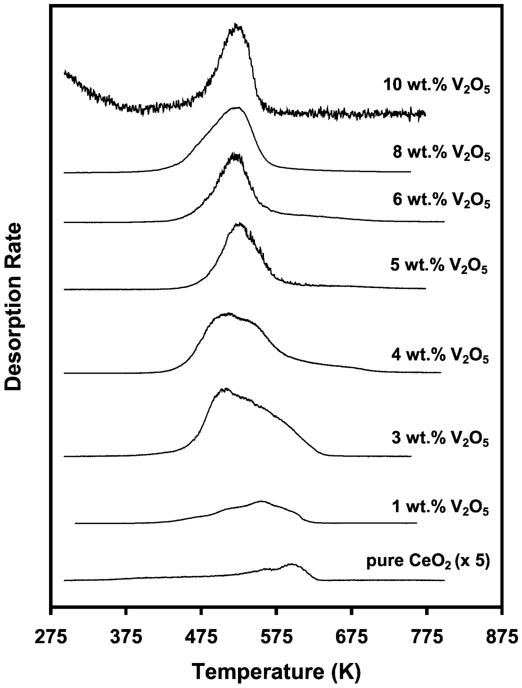


Fig. 4. CH_2O desorption spectra obtained during TPD with CH_3OH-dosed samples as a function of the vanadia weight loading. The spectra have been normalized to take into account variations in sample mass.

were studied. As shown in Fig. 3, for vanadia loadings less than 4 wt% the CO desorption spectrum contained a single peak centered at 615 K. This peak temperature is close to that observed for CO desorption from CH_3OH-dosed polycrystalline CeO_2. Thus, this feature can be attributed to the oxidation of methoxide intermediates that reside on the ceria support. The observation that the intensity of this peak decreases with increasing vanadia coverage is consistent with this assignment. The near absence of the CO peak due to reaction of methoxides on the ceria support for vanadia loadings greater than 5 wt% indicates that this loading corresponds to approximately monolayer vanadia coverage. For the ceria support used in this study, which had a surface area of 35 m^2/g, this corresponds to 9.5 V $atoms/nm^2$ in the vanadia monolayer. This value is a little higher than the 8 V $atoms/nm^2$ reported by Burcham and Wachs for monolayer coverage of vanadia on ceria [23]. For vanadia loadings between 5 and 8 wt%, the CO desorption spectra contain two small peaks centered at 530 and 600 K, while only the low-temperature peak is present in the spectrum from the 10 wt% sample.

The H_2CO desorption spectra as a function of vanadia loading displayed in Fig. 4 show that for monolayer or slightly higher vanadia coverages, H_2CO is produced in a single peak centered at 525 K. For lower vanadia coverages, the formaldehyde desorption curves are more complex and appear to contain three overlapping peaks centered at 515, 550, and 605 K. The position of the high-temperature peak is close to that for production of formaldehyde on the pure CeO_2 sample and can, therefore, be attributed to the reaction of methoxide intermediates on the support. The remaining peaks at 515 and 550 K are due to reaction on the vanadia. The appearance of two separate H_2CO peaks indicates that there are multiple reaction channels for the production of this product.

In our previous TPD studies of the reaction of CH_3OH on polycrystalline V_2O_5/TiO_2, multiple H_2CO desorption peaks were also observed [18]. In that case it was demonstrated that the H_2CO peak position correlated with the oxidation state of the vanadium cations in the supported vanadia layer. Similar results have also been reported in studies of the reactivity of vanadia monolayers supported on both $CeO_2(111)$ and $TiO_2(110)$ single crystal surfaces [16,17,24]. In these studies it was found that the temperature at which dehydrogenation of adsorbed methoxide intermediates to produce CH_2O occurred during a CH_3OH TPD experiment was a function of the oxidation state of the cations in the vanadia layer. This is illustrated in Fig. 5 which shows two TPD spectra obtained in our earlier study [16] of a 0.5 monolayer VO_x film on $CeO_2(111)$. The upper portion of the figure shows the formaldehyde desorption spectra obtained from a CH_3OH-dosed 0.5 monolayer vanadia film that contained exclusively V^{3+} as determined by XPS. For this sample the CH_2O peak is centered at 605 K. The CH_2O desorption spectrum in the lower half of the figure which contains a peak centered at 540 K was obtained from a CH_3OH-dosed 0.5 monolayer vanadia film that contained predominantly V^{5+} and a small fraction of V^{4+} as determined by XPS. These previous results suggest that the multiple CH_2O peaks in the TPD spectra from CH_3OH-

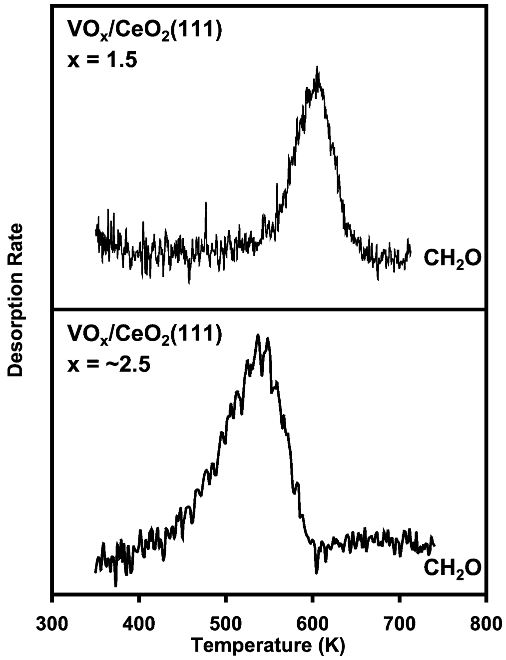


Fig. 5. H_2CO desorption spectra obtained from CH_3OH-dosed 0.5 monolayer vanadia film supported on a $CeO_2(111)$ single crystal. In the upper panel the vanadium cations were exclusively in the 3+ oxidation state and in the lower panel they were predominantly in the 5+ oxidation state. These data are from Ref. [16].

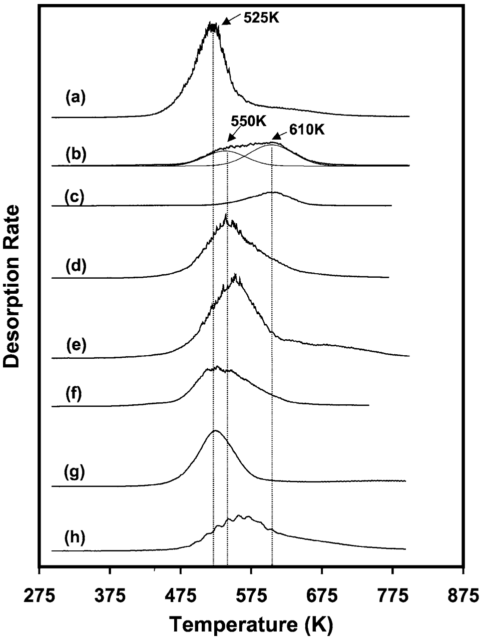


Fig. 6. CH_2O desorption spectra obtained from CH_3OH-dosed, 6 wt% V_2O_5/CeO_2 following various sample pretreatments: (a) freshly prepared sample annealed at 475 K in vacuum prior to the TPD run, (b) subsequent TPD run with the sample used in (a), (c) subsequent TPD run with the sample used in (b), (d) after reoxidation of the sample used in (c) in 0.1 Torr O_2 at 300 K, (e) after reoxidation of the sample used in (c) in 0.1 Torr O_2 at 475 K, (f) after reoxidation of the sample used in (c) in 0.1 Torr O_2 at 750 K, (g) after reoxidation of the sample used in (c) in 1 Torr O_2 at 750 K, (h) freshly prepared sample annealed at 750 K in vacuum prior to the TPD run.

dosed polycrystalline vanadia/ceria samples are also due to reaction of methoxide intermediates on V sites with different oxidation states. In order to provide additional evidence for this conclusion, a series of CH_3OH TPD experiments were performed with a 6 wt% sample in which the pretreatment conditions were varied in order to alter the distribution of the oxidation states of the vanadium cations in the supported vanadia layer. Formaldehyde desorption spectra obtained in this series of experiments are displayed in Fig. 6.

Curve (a) in Fig. 6 corresponds to the CH_2O desorption spectrum obtained in a CH_3OH TPD run from a freshly prepared sample that had been briefly annealed at 475 K prior to the experiment (this is the same curve as that for the 6 wt% sample in Fig. 4). As described above, the CH_2O desorption curve for this sample contained a single peak centered at 525 K. Curve (b) was obtained in the subsequent CH_3OH TPD run and is substantially different from that obtained from the fresh sample. The CH_2O desorption curve for this run consists of two overlapping peaks centered at 550 and 610 K. The total area of the CH_2O peaks also decreased from run one to run two. Curve (c) was obtained in a subsequent CH_3OH TPD run with the sample used for curve (b). This desorption spectrum contains a single, small peak at 610 K.

Since the oxidation of methanol to formaldehyde is accompanied by reduction of the vanadia layer, the sample becomes increasingly reduced with each TPD run. Thus, the changes in the CH_2O desorption spectra as a function of the number of TPD runs can be attributed to changes in the extent of reduction of the vanadia layer. The effect of reoxidizing samples that had previously been reduced via several CH_3OH TPD runs (i.e., samples which exhibit CH_2O desorption curves similar to that of curve (c) in Fig. 6) was also studied. The oxidation treatments varied from exposure to 0.1 Torr of O_2 for 10 min at 300 K (curve (d)), 475 K (curve (e)), and 750 K (curve (f)) to exposure to 1 Torr of O_2 for 10 min at 750 K (curve (g)). (For the samples annealed at elevated temperatures the O_2 was evacuated after they had cooled to room temperature.) In this series of experiments the low-temperature CH_2O peaks grow in intensity while that of the high-temperature peak decreases in intensity as the strength of the oxidation treatment is increased. Exposure to 1 Torr of O_2 at 750 K was required in order to obtain a sample which exhibited a CH_2O desorption curve similar to that obtained from the fresh sample.

The effect of annealing a sample in vacuum at 750 K on CH_2O production during a CH_3OH TPD experiment was also investigated. Curve (h) in Fig. 6 was obtained from a sample pretreated in this manner. Note that high-temperature CH_2O desorption peaks are observed in this data set, suggesting that annealing to 750 K in vacuum also results in partial reduction of the vanadia layer.

3.3. Calorimetry

Calorimetry was used to measure the isosteric heat of reoxidation of partially reduced supported vanadia catalysts.

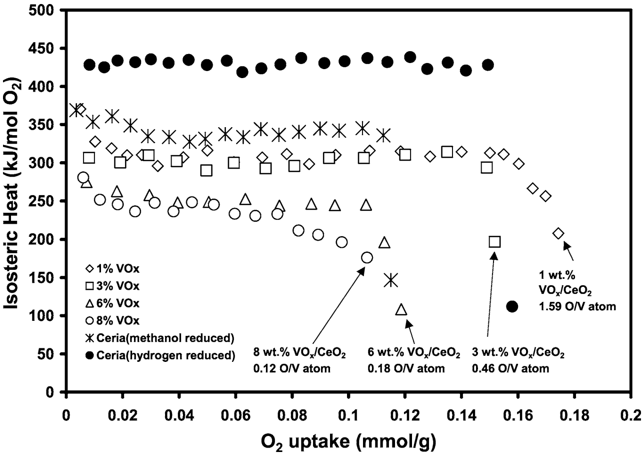


Fig. 7. Heat of adsorption of O_2 at 425 K for pure CeO_2 and 1, 6, 8, and 10 wt% V_2O_5/CeO_2. Pure ceria was reduced prior to the calorimetry measurements by annealing in hydrogen and methanol, respectively. Ceria-supported vanadia samples were reduced prior to the calorimetry measurements by annealing in 50 Torr of CH_3OH at 750 K.

Table 2
Isosteric heat of reoxidation of partially reduced supported vanadia catalysts

Sample	Reductant	Isosteric heat (kJ/mol) O_2
CeO_2	H_2	430 ± 10
CeO_2	CH_3OH	335 ± 10
1 wt% V_2O_5/CeO_2	CH_3OH	305 ± 10
3 wt% V_2O_5/CeO_2	CH_3OH	305 ± 10
6 wt% V_2O_5/CeO_2	CH_3OH	245 ± 10
8 wt% V_2O_5/CeO_2	CH_3OH	245 ± 10

The isosteric heat per mole of O_2 adsorbed is plotted in Fig. 7 for samples with vanadia loadings of 1, 3, 6, and 8 wt%. The measured isosteric heats of reoxidation of partially reduced supported vanadia are also listed in Table 2. In order to partially reduce the supported vanadia layer the samples were exposed to 50 Torr of CH_3OH for 10 to 15 min, the system was then evacuated, and the sample was heated to 750 K at a rate of 15 K/min. For comparison purposes data for two pure ceria samples, one reduced by annealing in H_2 and one reduced by annealing in CH_3OH, were also collected. Note that there is a large difference in the heats of reoxidation for these two samples: 430 ± 10 kJ/mol of O_2 for the H_2-reduced sample and 335 ± 10 kJ/mol of O_2 for the CH_3OH-reduced sample. The H_2-annealed sample required more oxygen to be completely reoxidized compared to the CH_3OH-annealed sample. Thus, the H_2 treatment resulted in a higher extent of reduction compared to the CH_3OH treatment. It is possible that the CH_3OH treatment resulted in only surface reduction, while the H_2 treatment led to partial reduction of the bulk and this is responsible for the variation in the heats of reoxidation for the two different pretreatments.

The data for the CH_3OH-annealed pure ceria sample demonstrate that this pretreatment is sufficient to at least partially reduce the ceria support. This in turn complicates the analysis of the calorimetry data for the supported vanadia samples, since the measured heats will be an average of the heats for reoxidation of both the vanadia layer and the ceria support. The ratios of adsorbed oxygen to vanadium at saturation, which are given in the figure, confirm that this is indeed the case. For the 1 and 3 wt% samples the O/V ratios at saturation were 1.59 and 0.46, respectively. Both of these values are greater than what would be required assuming all the vanadium in each sample was initially V^{3+} and was completely oxidized to V^{5+}. The fact that the measured heats decrease with increasing vanadia coverage is also consistent with this conclusion. Note, however, that the isosteric heat of reoxidation reaches a limiting value of approximately 245 kJ/mol of O_2 for the 6 and 8 wt% samples. For these samples the ceria support is completely covered by vanadia and the measured heats should therefore more accurately reflect the reoxidation of the supported vanadia layer. These values are still approximate, however, since as will be shown below by XPS, the ceria support may still have been partially reduced.

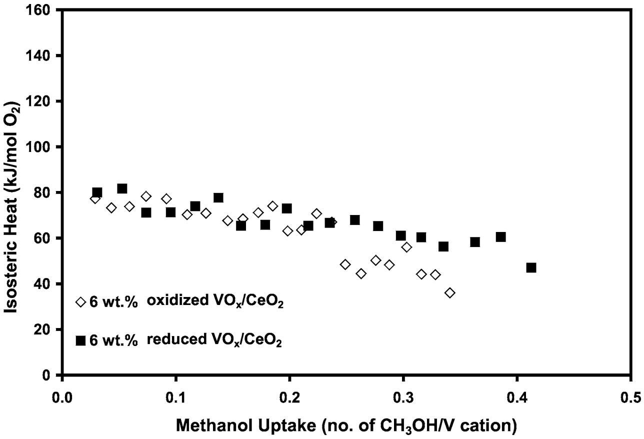
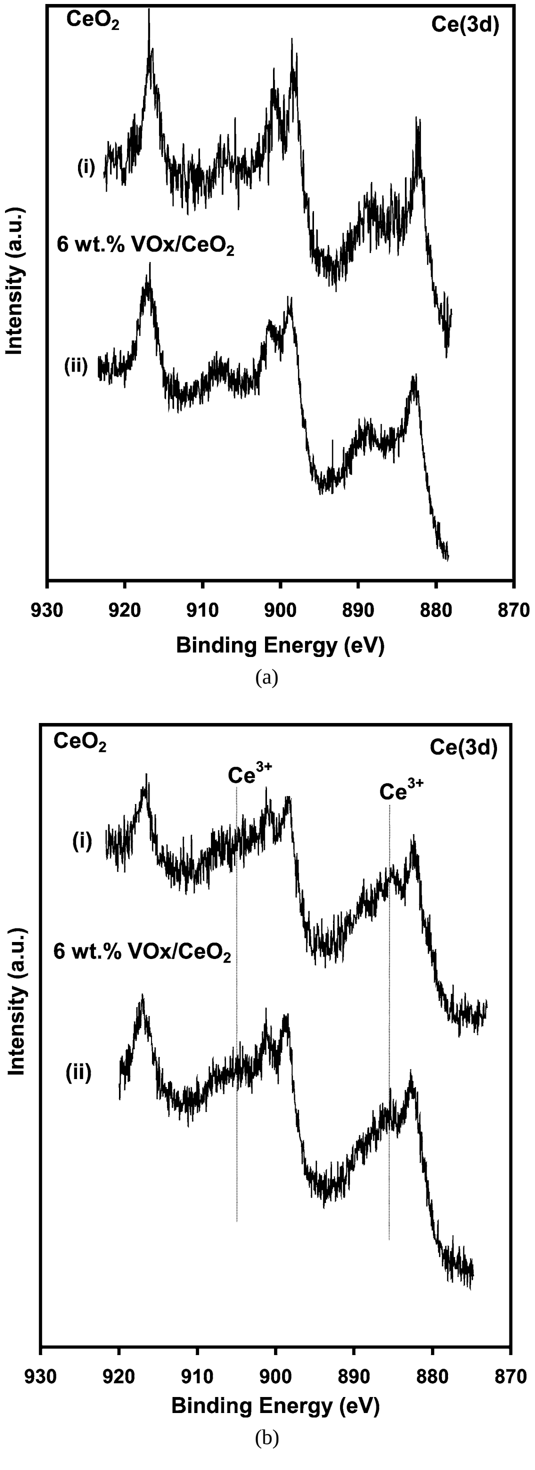


Fig. 8. Heat of adsorption of CH_3OH at room temperature on 6 wt% V_2O_5/CeO_2 and 6 wt% V_2O_3/CeO_2.

The heat of adsorption of methanol on both an oxidized and a reduced 6 wt% vanadia/ceria sample was also measured. The oxidation and reduction treatments used here were they same as those used in the calorimetry study of the heats of reoxidation. The results of this set of experiments are presented in Fig. 8. For both samples the heat of adsorption was approximately 80 kJ/mol at low CH_3OH coverages and decreased gradually with increasing coverage.

3.4. XP spectra of CeO_2-supported vanadium oxide

XPS was used to characterize the oxidation state of the cations in the vanadia layer and the ceria support as a function of sample pretreatment. Ce(3d) spectra for pure ceria and 6 wt% vanadia/ceria are displayed in Fig. 9. Part a of this figure contains spectra for fully oxidized samples (i.e., annealed in air at 775 K and then heated to 475 K in vacuum), while the spectra in part b were obtained immediately after a CH_3OH TPD experiment that was performed in the prechamber on the UHV system using conditions (i.e.,



(a)

(b)

Fig. 9. (a) Ce 3d XP spectra of (i) CeO_2 and (ii) 6 wt% VO_x/CeO_2. Spectra were obtained from freshly prepared, fully oxidized samples. (b) Ce 3d XP spectra of (i) CeO_2 and (ii) 6 wt% VO_x/CeO_2. These spectra were obtained following a CH_3OH TPD run.

CH_3OH dose and heating rate) similar to those used for the TPD studies. The Ce(3d) spectra are rather complex due to a variety of shakedown features. The reader is referred to papers by Creaser et al. [25] and Pfau and co-workers [26,27] for specific assignments of the various features in the Ce(3d) XP spectra. For this study, it suffices to point out that the spectra for both fresh samples are consistent with that reported in the literature for nearly stoichiometric CeO_2, i.e., Ce^{4+} [25,26,28]. As shown in part b of the figure, for both samples additional features appear in the Ce(3d) spectra following a CH_3OH TPD experiment. These changes can be attributed to a reduction of a portion of the Ce^{4+} to Ce^{3+}. Unfortunately, due to the complexity of the Ce(3d) spectra it is difficult to quantify the extent of reduction. Based on the peak shapes it appears, however, that the extent of reduction is similar for both the ceria and the vanadia/ceria samples.

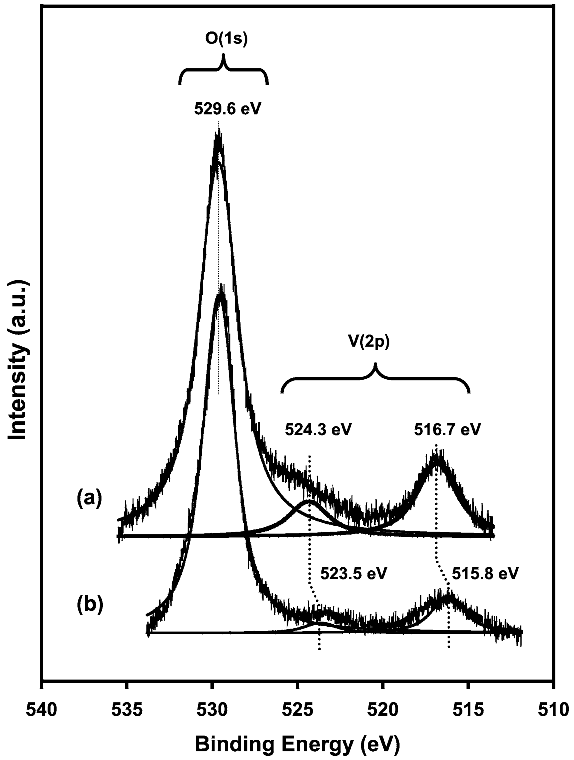


Fig. 10. O 1s and V 2p XP spectra for 10 wt% VO_x/CeO_2: (a) freshly prepared, fully oxidized samples and (b) after a CH_3OH TPD run.

XPS spectra of the O(1s) and V(2p) regions were also collected. As noted in Section 2 the V(2p) peaks overlap with Al-K_{α_3} and K_{α_4}-induced satellites of the O(1s) peak. For samples with monolayer or less vanadia coverage the intensity of the V(2p) peaks was similar to that of the O(1s) satellites. Upon subtraction of the satellites the V(2p) peaks were barely discernable above the noise level in the spectra. This, unfortunately, precluded accurate determination of the vanadium oxidation states for these samples. Such information could be obtained, however, from the spectra of the 10 wt% vanadia/ceria sample. The O(1s) and V(2p) region of the XP spectrum for this sample is displayed in Fig. 10. Spectrum (a) corresponds to a freshly prepared sample while spectrum (b) was obtained after a CH_3OH TPD experiment. The TPD experiment was again performed with the sample positioned in the prechamber on the UHV analysis system.

The large peak centered at 529.6 eV in each spectrum corresponds to the O(1s) peak of both the support and the vanadia film. The much smaller doublet that appears at lower binding energies can be assigned to the $V(2p_{1/2})$ and $V(2p_{3/2})$ states. For the fresh sample, the $V(2p_{3/2})$ peak is centered at 516.7 eV. This binding energy is close to that reported in [29] for V^{5+} and confirms that the vanadia is fully oxidized. As shown in spectrum (b), following the CH_3OH TPD experiment both V(2p) peaks shift to lower binding energies. The $V(2p_{3/2})$ peak is centered at 515.8 eV in this spectrum. This binding energy is consistent with that reported in the literature for V^{3+} [29,30]. As shown by the curve fits in the figure, the $V(2p_{3/2})$ spectrum contains a shoulder toward higher binding energies. This indicates that some V^{4+} or possibly V^{5+} is also present in this sample. These results further confirm that the vanadia layer undergoes reduction during the CH_3OH TPD experiment. Since 10 wt% vanadia is above monolayer coverage, one needs to be a little cautious in extrapolating this result to the mono and submonolayer coverage samples. Note, however, that this result is identical to that obtained in our previous studies of submonolayer vanadia films supported on $CeO_2(111)$ [15]. The use of a single crystal support in the previous study facilitated the collection of much higher quality XPS spectra.

4. Discussion

The TPD and XPS results obtained in this study indicate that the activation energy for the dehydrogenation of adsorbed methoxides to produce formaldehyde on vanadia/ceria is a function of the oxidation state of the vanadium cations in the supported layer. On oxidized, monolayer vanadia films that contain predominantly V^{5+}, CH_2O is produced during CH_3OH TPD at 525 K, while on highly reduced vanadia layers that contain predominantly V^{3+}, this reaction occurs at 610 K. These assignments are consistent with those reported previously in a study of the reaction of methanol on a vanadia film supported on a $CeO_2(111)$ single crystal. In that study it was found that for $V_2O_5/CeO_2(111)$ and $V_2O_3/CeO_2(111)$ samples CH_2O was produced at 540 and 605 K, respectively, during CH_3OH TPD [16].

In addition to the CH_2O peaks at 525 and 610 K, which have been assigned to reaction on V^{5+} and V^{3+}, respectively, an additional CH_2O peak was observed during CH_3OH TPD in the present study centered at 550 K. In light of the assignments of the other two peaks it is plausible that this peak is due to reaction on V^{4+}. This assignment is consistent with the XPS results in Fig. 10, which indicate that the reduced sample contains a range of vanadium oxidation states. In our previous TPD study of the reaction of CH_3OH on $VO_x/CeO_2(111)$ an intermediate temperature CH_2O peak at 550 K was not resolved [15,16]. There is some evidence, however, that suggests that an intermediate temperature CH_2O peak may have also been present in the TPD data obtained in that study. For $V_2O_3/CeO_2(111)$, CH_2O was produced during TPD in a narrow peak centered at 605 K. It was shown that this peak could be fit using first-order kinetics, a preexponential factor of $10^{13}\ s^{-1}$ and an activation energy of 158 kJ/mol. For the $V_2O_5/CeO_2(111)$ sample, CH_2O was produced in a much broader peak centered at 540 K. An adequate fit to this peak required the use of an unusually low preexponential factor of $2 \times 10^7\ s^{-1}$ and an activation energy of 83.7 kJ/mol. It was pointed out, however, that the broad nature of this peak might have been due to the presence of both V^{4+} and V^{5+}. The results of the present study suggest that this was indeed the case. Since individual peaks for V^{4+} and V^{5+} cannot be resolved in the single crystal data it is not possible to use this data to accurately determine the kinetic parameters for the dehydrogenation of methoxides on V_2O_5/CeO_2. If one assumes a preexponential factor of $10^{13}\ s^{-1}$, an estimate for the activation energy can be obtained, however, using the CH_2O peak temperature from the polycrystalline samples. This gives an activation energy for dehydrogenation of adsorbed methoxides of 147 kJ/mol.

The partial oxidation of methanol to formaldehyde on supported vanadia is generally thought to proceed via the following Mars-Van Krevelen-type mechanism in which methanol adsorbs dissociatively on a surface vanadium site to form an adsorbed methoxide and hydroxyl group [reaction (1)] [12,23,31]. The methoxide then undergoes dehydrogenation to produce gaseous formaldehyde in the rate-determining step. This step proceeds either via hydride transfer to an adjacent vanadium center [as indicated in reaction (2)] or via proton transfer to a nearby oxygen. The remaining steps involve the reaction of hydroxyl groups to produce water and reoxidation of the vanadium site

$$CH_3OH + V^* + O^* \Leftrightarrow V^*\text{–}OCH_3 + O^*\text{–}H, \tag{1}$$

$$V^*\text{–}OCH_3 \Rightarrow CH_2O + V^*\text{–}H, \tag{2}$$

$$V^*\text{–}H + O^*\text{–}H \Leftrightarrow V^\bullet + H_2O + \square, \tag{3}$$

$$O_2 + 2\square \Leftrightarrow 2O^*. \tag{4}$$

($\square$, V^*, O^*, and $V^\bullet$ correspond to an oxygen vacancy, a fresh vanadia site, an oxygen site, and a reduced vanadia site, respectively.)

The rate expression based on this mechanism and the assumption of a low surface methoxide concentration is as follows [12,31,32]:

$$\mathrm{TOF} = k_{\text{apparent}} \times \frac{P_{CH_3OH} P_{O_2}^{1/4}}{P_{H_2O}^{1/2}},$$

where $k_{\text{apparent}} = (K_1 K_3^{1/2} K_4^{1/4}) \times k_{\text{rds}}$.

The apparent activation energy for this rate expression is given by the following equation:

$$E_{\text{app}} = E_{\text{rds}} + \Delta H_1 + \tfrac{1}{2}\Delta H_3 + \tfrac{1}{4}\Delta H_4.$$

If step (2) of the reaction occurs via proton transfer rather than hydride transfer identical expressions for TOF and E_{app} are obtained except that ΔH_3 corresponds to reaction of two O*–H species rather than an O*–H and a V*–H. Several previous studies of the kinetics of partial oxidation of methanol on vanadia/ceria have reported values for E_{app} near 84 kJ/mol [9,23,33]. To provide insight into the origin of the support effect for supported vanadia catalysts it would be useful to determine how the various contributions to E_{app}, especially E_{rds}, vary as a function of the identity of the support. Unfortunately, using overall rate data it is generally not possible to separate out each contribution. The techniques used in the present study, however, have allowed two of the parameters, E_{rds} and ΔH_1 (the heat of adsorption of methanol) to be directly measured and a third ΔH_4 (the heat of reoxidation of the vanadia layer) to be approximated. As noted above for monolayer V_2O_5/CeO_2, E_{rds}, and ΔH_1 were determined to be 147 and 80 kJ/mol, respectively.

The heat of reoxidation of a partially reduced vanadia monolayer was found to be 245 kJ/mol and this value can be used as a first-order approximation of ΔH_4. It is useful, however, to consider what this number actually corresponds to in a little more detail. Following the CH_3OH reduction treatment used in the calorimetry study the TPD and XPS data indicate that the 6 and 8 wt% samples initially contained a mixture of V^{3+} and V^{4+}. The TPD data also shows that exposing a reduced 6 wt% sample to O_2 at 475 K results in a sample that contains predominantly V^{4+} and some V^{5+}. Thus, the measured heat is most likely an average for the oxidation of V^{3+} to V^{4+} and V^{4+} to V^{5+}. It is interesting to compare this result to that predicted by thermodynamics for bulk vanadium oxides. The heats of oxidation of V_2O_3 and V_2O_4 at 425 K, the temperature at which the calorimetry measurements were carried out, are as follows [34]:

$$2V_2O_3 + O_2 \to 2V_2O_4, \quad \Delta H = -379\ \mathrm{kJ/mol\ of\ } O_2,$$

$$2V_2O_4 + O_2 \to 2V_2O_5, \quad \Delta H = -306\ \mathrm{kJ/mol\ of\ } O_2.$$

This shows that for the bulk oxides the ΔHs for the oxidation of both V^{3+} to V^{4+} and V^{4+} to V^{5+} are significantly greater than the average value measured for monolayer VO_x/CeO_2. Thus, the vanadium–oxygen bond strengths in supported vanadia appear to be less than those in the bulk oxides. This conclusion is consistent with the fact that the monolayer species are much more active oxidation catalyst than the bulk oxides.

We have previously reported similar measurements for vanadia supported on TiO_2. Based on TPD results from $V_2O_5/TiO_2(110)$, E_{rds} was estimated to be 125 kJ/mol [35] and calorimetry measurements with polycrystalline VO_x/TiO_2 give an approximate value for ΔH_4 of −240 kJ/mol [18]. These values are only slightly smaller than those reported here for V_2O_5/CeO_2. Based on these results one might expect V_2O_5/CeO_2 and V_2O_5/TiO_2 to have similar overall reactivities for the oxidation of methanol to formaldehyde. The published turnover frequencies for methanol oxidation on supported vanadia indicate that this is indeed the case [10]. In order to provide more insight into the origin of the support effect similar measurements are currently being made for vanadia monolayers on several other metal oxide supports.

It is useful to consider how the results obtained in this study may provide some insight into the mechanism of the dehydrogenation of adsorbed methoxides to produce formaldehyde. As noted above, two different mechanisms for this rate-determining step have been proposed, proton transfer and hydride elimination [10,12,24,36,37]. In the former, dehydrogenation of the methoxide proceeds via transfer of a proton from the methyl group of the methoxide to a basic bridging or terminal oxygen in the supported vanadia layer. While in the latter, the reaction can be described as a β-hydride elimination in which the hydride is transferred to a vanadium ion. Recently, Oyama et al. [12] have argued in favor of the hydride transfer mechanism based on the grounds that this pathway is more consistent with oxidation being a loss of electrons from the organic species and a gain of electrons by the metal ion. Furthermore, Oyama et al. have suggested based on NEXAFS data that the activity for methanol oxidation to formaldehyde correlates with the density of electron-accepting states on the metal center and that this may be the origin of the support effect for supported monolayer oxide catalysts. Hydride elimination is also consistent with predictions obtained in several theoretical studies [38,39].

It is possible that the dependence of the activation energy for the dehydrogenation of the adsorbed methoxide on the oxidation state of the vanadium cations may also provide some clues into the mechanism and transition state for this reaction. In our previous methanol TPD studies with $VO_x/CeO_2(111)$ a kinetic isotope effect was observed for the CH_2O desorption peak on both $V_2O_5/CeO_2(111)$ and $V_2O_3/CeO_2(111)$ confirming that C–H bond breaking is the rate-limiting step in both cases [16]. In the present study it was shown that the heat of adsorption of CH_3OH on supported V_2O_3 and V_2O_5 monolayers was approximately 80 kJ/mol. This result along with the activation energies for the dehydrogenation step that were estimated from the TPD peak temperatures allows an energy versus reaction coordinate diagram to be constructed for this system. Such a diagram is displayed in Fig. 11. This diagram serves to illustrate the point that since the heat of adsorption does not depend on the vanadium oxidation state, the variation in the activation energy must be due to differences in the stability of the transition state.

Since the C–H bond-breaking reaction takes place at a position β to the vanadium cation, the influence of the vanadium oxidation state on the energetics of the transition state may be analogous to similar substituent effects that have been reported in the literature for β-hydride elimination from alkoxides adsorbed on Cu and Ag surfaces. For example, Gellman and Dai have used TPD to study the energetics of the dehydrogenation of a series of fluorinated ethoxides ($F_nCH_{3-n}CH_2O$, $n = 0$–3) on Cu(111) [40]. The TPD peak temperatures for the fluorinated acetaldehyde products were used to determine the activation energies for the dehydro-

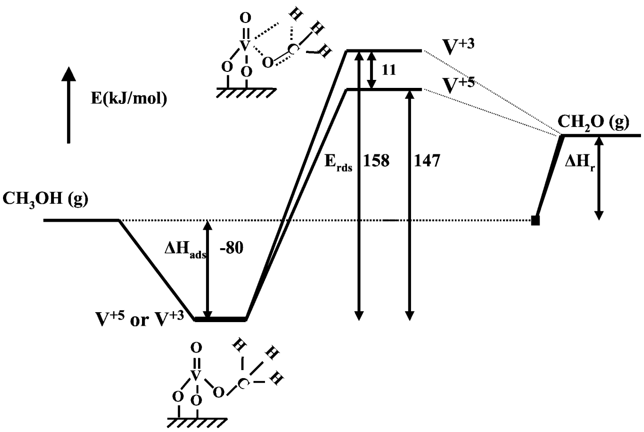


Fig. 11. Potential energy diagram for the reaction of CH_3OH to CH_2O on vanadia/ceria.

genation reaction. It was observed that increasing the electronegativity of the methyl group by increasing the extent of fluorination produced a systematic increase in the activation energy. It was argued that increasing the electronegativity of the methyl group would serve to destabilize a transition state in which there is a positive charge on the β-carbon. This would be the case if the reaction proceeds via hydride transfer since the transition state would be of the form $C^{\delta+}\cdots H^{\delta-}$.

In the present study changing the oxidation state of the vanadium cation from 3+ to 5+ should have an effect similar to that of increasing the extent of fluorination of the methyl group in an adsorbed ethoxide. In both cases these changes result in an increase in the electronegativity of a group that is adjacent to the β-carbon where the dehydrogenation reaction takes place. Thus, if the dehydrogenation reaction proceeds via β-hydride elimination on supported vanadia, one might expect the trends in the activation energy for dehydrogenation of the methoxide with increasing vanadium oxidation state to mirror those observed when increasing the extent of fluorination of the methyl group in ethoxides on Cu(111). In the case of the supported vanadia, however, the effect is just the opposite: the activation energy decreases as the vanadium oxidation state increases. It is tempting to interpret this result as evidence that the reaction does not proceed via β-hydride elimination. Indeed it could be argued that the observed trend is consistent with a transition state in which there is a negative charge on the β-carbon (i.e., $C^{\delta-}\cdots H^{\delta+}$) and, therefore, the reaction proceeds via proton transfer. This argument, however, does not take into account the fact that if the reaction proceeds via β-hydride elimination two separate vanadium cations are involved in the transition state: one to which the methoxide is bonded and a second which receives the transferred hydride. The increase in the electronegativity of this second V cation with increasing oxidation state would have a stabilizing effect on the transition state for hydride transfer and cause a decrease in the activation energy. Since this V cation is directly involved in the reaction, its influence on the energetics may be significantly greater than that of the vanadium cation to which the methoxide is bonded, especially if the reaction proceeds through a late transition state, which is generally thought to be the case for β-hydride elimination from alkoxides.

Unfortunately, the current study does not provide a definitive answer to the question as to whether the reaction proceeds via hydride transfer or proton transfer. Thus, the latter explanation for the influence of the vanadium oxidation state on the energetics of the reaction is still somewhat speculative. The Gellman work, however, suggests a set of experiments that may provide an answer to this question. If the reaction proceeds via β-hydride elimination, the trends observed by Gellman and Dai with fluorinated ethoxides on Cu(111) should also occur on supported vanadia, i.e., the activation energy for dehydrogenation of the ethoxide should increase with the extent of fluorination of the methyl group. These experiments do not require that the vanadium oxidation state be varied and can be performed independently on V_2O_3/CeO_2 and V_2O_5/CeO_2. We are currently carrying out such a study, the results of which will be the subject of a future publication.

5. Conclusions

The TPD results obtained in this study demonstrate that the activation energy for the dehydrogenation of adsorbed methoxide intermediates to produce formaldehyde on vanadia/ceria is a function of the oxidation state of the vanadium cations in the supported layer. During TPD with methanol-dosed vanadia/ceria samples, formaldehyde was produced at three separate temperatures, 525, 550, and 610 K, depending on the pretreatment conditions. TPD and XPS data in conjunction with comparisons to previous studies employing single crystal ceria supports indicate that these peaks correspond to reaction of methoxide species adsorbed on V^{5+}, V^{4+}, and V^{3+}, respectively. Based on the TPD results the activation energy for this reaction was estimated to be 147 kJ/mol on V^{5+} and 158 kJ/mol on V^{3+}. Calorimetry measurements showed that the vanadium oxidation state did not affect the heat of adsorption of methanol, which was 80 kJ/mol on both V_2O_5/CeO_2 and V_2O_3/CeO_2. Together these results demonstrate that a lower vanadium oxidation state destabilizes the transition state for the dehydrogenation reaction. Calorimetry measurements also showed that the heat of reoxidation of monolayer vanadia/ceria catalyst that had been reduced by annealing in methanol was 245 ± 10 kJ/mol of O_2, which is similar to that reported for vanadia/titania.

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