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TPD–TGA and Calorimetric Study of the Partial Oxidation of Methanol on TiO_2-Supported Vanadium Oxide

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The partial oxidation of methanol to formaldehyde on titania-supported vanadium oxide was studied using temperature-programmed desorption (TPD) and thermal gravimetric analysis (TGA). Calorimetry was also used to measure the heats of reoxidation of partially reduced vanadia/titania catalysts. The TPD results showed that the activation energy for the oxidation of adsorbed methoxides to formaldehyde depends on the extent of reduction of the supported vanadia layer. On supported V_2O_5 and V_2O_3 formaldehyde was produced at 535 and 630 K, respectively. The TPD results also demonstrated that the thermal stability of the supported vanadia was coverage dependent and suggested that polyvanadate species are more thermally stable than isolated vanadyls. The heat of reoxidation of partially reduced supported vanadia layers was measured calorimetrically and found to be 240 ± 10 kJ/mol of O_2.

INTRODUCTION

Supported vanadia catalysts, such as vanadia/titania, exhibit high activity and selectivity for a variety of reactions, including the oxidation of *o*-xylene to phthalic anhydride and methanol to formaldehyde and the oxidative dehydrogenation of alkanes (1–4). Over the last two decades these catalysts have been the subject of numerous studies (1–14), which have provided much insight into their structure and the origin of their unique reactivity. It is now well established that the active phase of the vanadia consists of monolayer or submonolayer coverages of isolated and/or polymerized VO_4 units in direct contact with the support (5–7, 12). Although the structure of the vanadia species appears to be largely independent of the identity of the support, the support still strongly influences the overall reactivity (12, 14). Based in large part on this observation it has been suggested that oxygens that bridge the support and the vanadium cations are directly involved in the oxidation reactions (2, 8, 14).

Even though much is known about the structure of supported vanadia and the overall kinetics of reactions taking place on these catalysts, a fundamental understanding of the origins of their unique reactivity is still lacking. For example, the thermodynamic properties of supported vanadia, including the vanadium–oxygen bond strengths, have yet to be measured. Although a large body of kinetic data can be found in the literature and the overall kinetics of many reactions on supported vanadia have been studied in detail, the reaction mechanisms and kinetic parameters for individual elementary steps that take place on supported vanadia have also in most cases not been elucidated. In the work presented here we have used a combination of temperature-programmed desorption (TPD) and calorimetry in an effort to provide additional insight into both the thermodynamic properties of vanadia supported on titania and the mechanism and kinetic parameters for the oxidation of methanol to formaldehyde on these catalysts. This work is complimentary to recent ultra-high vacuum TPD studies of the reaction of methanol on well-defined model catalysts consisting of mono- and submonolayer films of vanadia supported on single-crystal $TiO_2(110)$ (15, 16) surfaces and allows direct connections to be made between the reactivity of the model and high-surface-area catalysts.

EXPERIMENTAL

Sample Preparation

The incipient-wetness impregnation method was used to synthesize the vanadia–titania catalysts used in this study. Anatase TiO_2 (Degussa P-25) was used as the support and had a surface area of 52 m^2/g, as determined by the BET method. The support was calcined in air at 750 K prior to impregnating with an aqueous solution containing 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 total amount of impregnation solution was adjusted in order to produce catalysts with vanadia weight loadings between 1 and 20%. Subsequent to impregnation the samples were dried overnight at 400 K and then calcined in air at 775 K for 5 h. This synthesis method is similar to that which has been used in previous studies of vanadia–titania catalysts (10, 17–19).

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TPD–TGA

The TPD–TGA study was performed in a stainless-steel, diffusion-pumped, high-vacuum system equipped with a quadrupole mass spectrometer (VG) and a Cahn model 1000 microbalance. The background pressure in the system was $\sim 10^{-6}$ Torr. Samples were placed in a small tantalum pan that hung by a thin wire from the microbalance. The hanging pan assembly was enclosed in a quartz thimble that was attached to the stainless-steel housing of the microbalance. The sample was heated radiantly using a tube furnace, which was placed over the quartz thimble. The temperature was monitored using a thermocouple that was placed inside the tube furnace.

In most cases after being placed into the TPD–TGA system the vanadia–titania sample was pretreated by heating in vacuum to 500 K in order to remove adsorbed water, surface hydroxyls, and other weakly adsorbed impurities. For a TPD–TGA experiment the catalyst was initially exposed to ~15 Torr of methanol vapor at room temperature. The exposure time varied somewhat from run to run but was long enough to insure 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 750 K at a rate of 15 K/min. While heating, the desorbing species were monitored using the mass spectrometer and the sample mass was monitored using the microbalance. Multiple m/e ratios were collected during each TPD–TGA 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 the procedure described by Ko *et al.* (20).

Calorimetry

A custom-built calorimeter was used in this study. The design of the calorimeter was similar to that described by Parrillo *et al.* (21, 22). The calorimeter contained a hollow Pyrex cube sample holder that was connected to a Pyrex tube. Each of the five external faces of the cube (the sixth was attached to the tube) was covered with a thermocouple-based thermal flux meter (International Thermal Instrument Company). The output signals from the five flux meters were connected in series and monitored using a PC-based data acquisition system. The cubic sample cell and flux meters were placed in a large Al block that served as a heat sink. This whole assembly was contained in an oven and could be heated to temperatures up to 550 K. The sample holder assembly was also connected to a gas handling system that could be evacuated using a mechanical roughing pump. The gas handling system contained capacitance manometers that were used to monitor the pressure above the sample and a gas injection loop and associated valve that allowed for a known quantity of gas to be pulsed into the sample cell.

Approximately 2 mg of the vanadia–titania catalyst was used in each calorimetry experiment. In order to allow for better comparison between the TPD–TGA and calorimetric data, the sample pretreatment conditions used in the calorimetric studies were similar to those used in the TPD–TGA studies. A fresh catalyst sample was first heated to 500 K in vacuum to remove the adsorbed water. After cooling to room temperature the sample was exposed to methanol vapor and heated to 750 K at a rate of 15 K/min. The heat of adsorption of oxygen on the sample for a series of small O_2 pulses was then measured with the sample held at 425 K.

RESULTS

CH_3OH TPD–TiO_2

Before presenting the data for the reaction of methanol on the vanadia–titania samples the reaction of methanol on the TiO_2 support is discussed. TPD spectra for methanol-dosed titania are displayed in Fig. 1. At temperatures below 600 K the only desorbing species detected was the parent molecule, methanol, which desorbed in a broad peak centered at 500 K. It is possible that water also desorbed in this temperature range. Unfortunately, due to the high background level of water in the vacuum system it was not possible to collect H_2O desorption spectra using the same

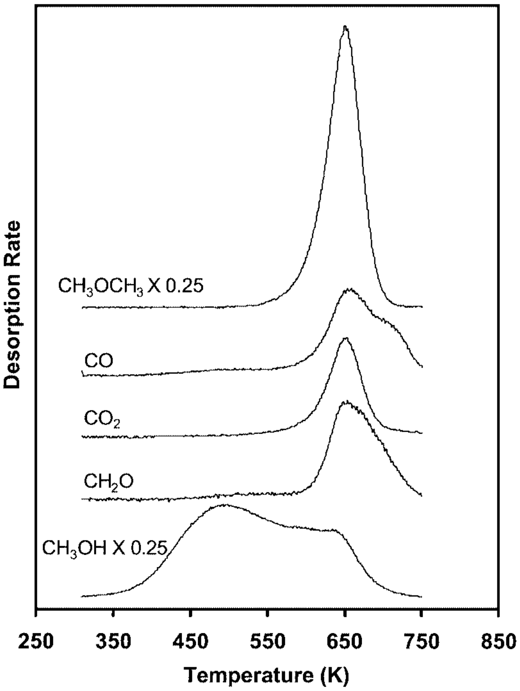

FIG. 1. TPD spectra obtained from CH_3OH-dosed TiO_2.

TABLE 1

Relative Yields of Carbon-Containing Products

Sample	Relative yield (%)			
	$(CH_3)_2O$	CO_2	CO	H_2CO
TiO_2	67.5	6.3	13.1	13.1
1 wt% V_2O_5/TiO_2	10.6	7.0	33.6	48.7
4 wt% V_2O_5/TiO_2	1.6	12.6	43.8	42.0
10 wt% V_2O_5/TiO_2	—	8.3	22.6	69.1

mass spectrometer gain as that used for the other products. Water desorption was, therefore, not monitored for during the TPD experiments. Based on the CH_3OH peak temperature and previous FTIR studies of the interaction of methanol with TiO_2 surfaces (23), the methanol peak can be assigned to the recombinative desorption of surface methoxides and hydroxyl groups. Both the methoxide and hydroxyl groups are formed via the dissociative adsorption of methanol at 300 K.

In addition to recombination with surface hydroxyls and desorption as methanol at 500 K, the TPD results demonstrate that a fraction of the adsorbed methoxides remain on the surface and react near 650 K to produce primarily dimethylether. Small amounts of the oxidation products, H_2CO, CO, and CO_2, are also produced at this temperature, as was CH_3OH. The relative yields of the carbon-containing products, excluding methanol, produced at 650 K are listed in Table 1. Note that titania is highly selective for the coupling of surface methoxides to form dimethylether. This pathway accounts for 67.5% of the products produced at 650 K. This result is consistent with that reported previously by Kim *et al.* (24) and Lusvardi *et al.* (25), who also used TPD to study the reaction of CH_3OH on titania. Steady state kinetic measurements for the oxidation of methanol on titania have also shown a high selectivity for the production of dimethylether (2).

Previous studies of the reaction of alcohols on rutile TiO_2 single crystals have demonstrated that only surfaces that contain Ti cations with multiple coordination vacancies are active for the bimolecular coupling of two alkoxides to form an ether (24, 25). Based on this observation it has been concluded that the two alkoxides involved in the ether-forming reaction reside on a single-surface Ti cation (24–27). The high selectivity for the formation of dimethylether obtained in the methanol TPD results, therefore, suggests that the surface of the titania sample used in this study contained a high number of oxygen defects and Ti cations with multiple coordination vacancies.

CH_3OH TPD–TGA—V_2O_5/TiO_2

Methanol TPD–TGA data were collected for a series of vanadia–titania catalysts. The specific vanadia loadings that were included in the series were 1, 2, 3, 4, 6, 7, and 10 wt%. In this series of experiments the catalyst samples were initially outgassed in the vacuum system for several hours at 300 K and then briefly annealed at 500 K in order to remove adsorbed water. After the samples had cooled back to room temperature the methanol TPD–TGA experiment was performed. Complete sets of TPD data for the 1, 4, and 10 wt% samples are displayed in Fig. 2. Product yields (excluding methanol) for these TPD runs are also listed in Table 1.

The TPD spectra for all vanadia coverages contain peaks for CH_3OH, CH_2O, CO, and CO_2. Dimethylether desorption was also observed for samples with low weight percents of vanadia. Molecular CH_3OH desorbed from all of the samples in a large peak centered at 460 K. For vanadia loadings less than 4 wt%, a second CH_3OH desorption peak centered at 580 K was also observed. The total amount of CH_3OH that desorbed intact was also significantly greater for samples with low weight percents of vanadia. As would be expected the methanol desorption features for samples with low vanadia coverages are similar to those in the TPD spectra for pure TiO_2. Thus, the high-temperature CH_3OH desorption peak can be assigned to recombinative desorption of methoxy species that reside on the TiO_2 support, while the low-temperature peak is due to desorption from both vanadia and exposed portions of the TiO_2 support.

As noted above, the production of dimethylether was only observed for samples with low coverages of vanadia. For the 1 wt% sample the dimethylether spectrum was

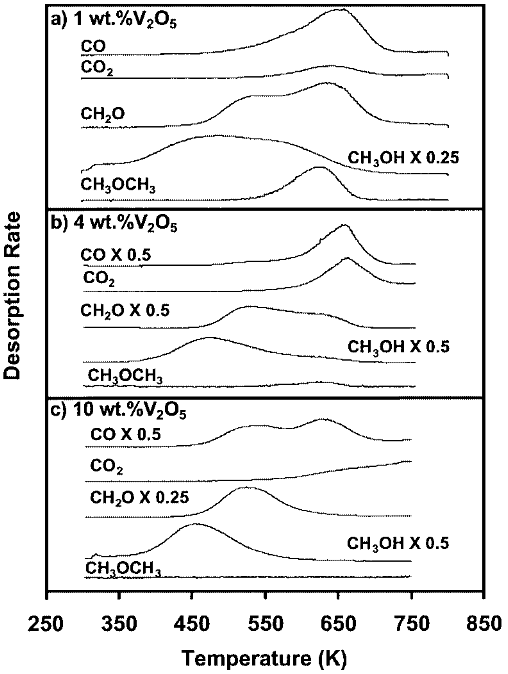

FIG. 2. TPD spectra obtained from CH_3OH-dosed 1, 4, and 10 wt% vanadia supported on titania.

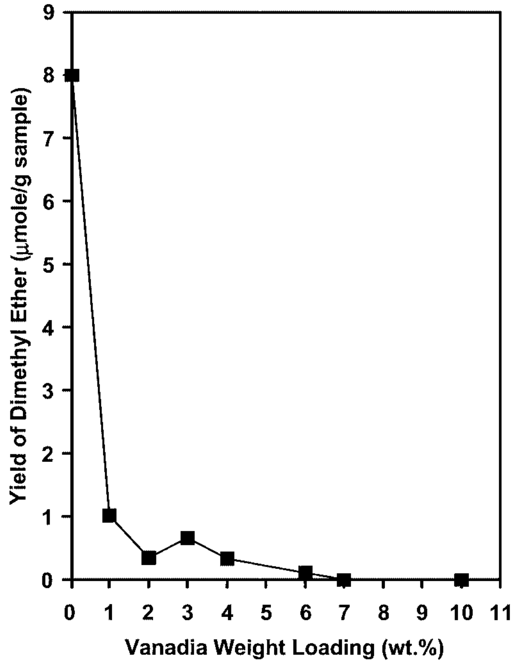

FIG. 3. Yield of dimethylether during a methanol TPD experiment as a function of the vanadia weight loading.

similar to that obtained from pure TiO_2 and contained a peak at 630 K. The normalized area of the dimethylether peak as a function of the vanadia loading is plotted in Fig. 3. As shown in this figure the area of the dimethylether peak decreased rapidly with increasing vanadia loading and was no longer observed for vanadia loadings of 7 wt% and greater. This result demonstrates that the bimolecular coupling of methoxy species to produce dimethylether takes place exclusively on the TiO_2 support and that the monolayer coverage of vanadia occurs between 6 and 7 wt%. This conclusion is consistent with that reported in the literature (2, 14, 28). For Example, Deo and Wachs have reported that 6 wt% vanadia corresponds to monolayer coverage for a titania support with a surface area of 50 m^2/g, which is close to that of the support used in this study (52 m^2/g) (2).

The shape of the plot of the amount of dimethylether produced versus vanadia loading (Fig. 3) shows that the decrease in the yield of dimethylether occurs very rapidly following the addition of relatively small amounts of vanadia. The area of the dimethylether peak for the 1 wt% vanadia sample was 88% less than that for the pure TiO_2. Since 1 wt% vanadia corresponds to roughly 0.15 monolayers, this decrease is much greater than what would be expected based on the fraction of the surface that is covered by vanadia. This result indicates that the vanadia selectively poisons the sites on the TiO_2 surface that are active for dimethylether production. As noted above, Ti cations with multiple coordination vacancies are the active sites for bimolecular coupling of alkoxides on TiO_2. These results, therefore, suggest that surface oxygen vacancies may be nucleation sites for vanadia deposits on the TiO_2 surface.

For low vanadia coverages both CO and CO_2 were produced near 650 K. The relative yield of these products goes through a maximum with increasing vanadia coverage, suggesting that they result from reactions taking place on both the vanadia and the TiO_2 support. A second CO desorption peak centered at 540 K also grows in with increasing vanadia coverage. Since this peak was not observed in the TPD data for the pure TiO_2 sample, it must be due to reaction on the vanadia.

The most important feature in the TPD data in Fig. 2 is the trend observed for formaldehyde production. For pure TiO_2, only small amounts of formaldehyde were produced. In contrast, for the vanadia–titania samples the relative yield of formaldehyde was much greater and for high-vanadia-weight loadings it was the primary product. Thus, as would be expected, the vanadia–titania samples are highly active for the oxidation of methanol to formaldehyde. For the 1 wt% vanadia sample, CH_2O desorbed in two overlapping peaks centered at 535 and 630 K. Increasing the vanadia coverage produced an increase in the total amount of CH_2O produced and an increase in the intensity of the low-temperature peak relative to the high-temperature peak. Only the peak at 535 K was observed in the spectrum for the 10 wt% vanadia sample. These trends can be seen more clearly in Fig. 4, which displays the formaldehyde desorption spectra for all of the vanadia coverages that were

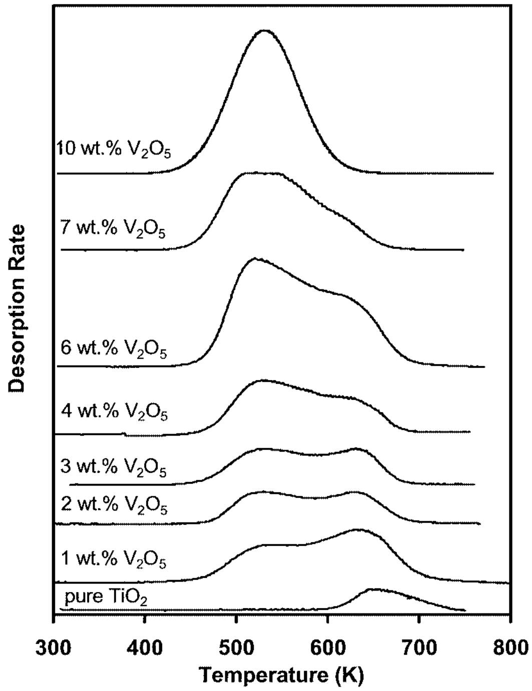

FIG. 4. Formaldehyde desorption spectra obtained during a methanol TPD experiment as a function of the vanadia weight loading. All the spectra have been normalized to take into account variations in sample mass.

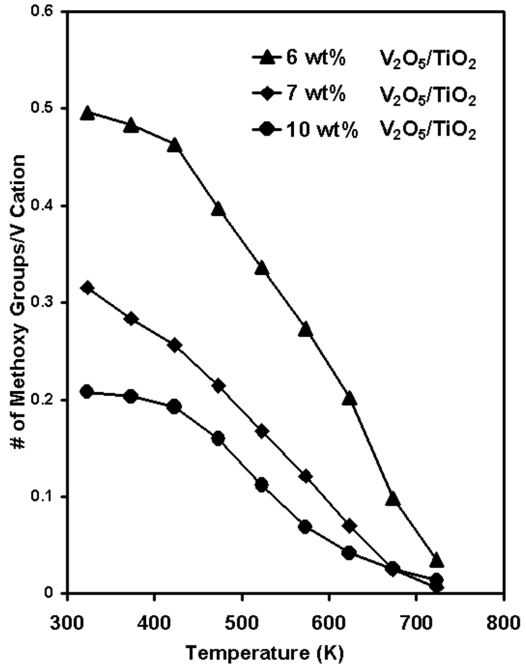

FIG. 5. Number of surface methoxy groups per vanadium cation as a function of temperature for CH_3OH-dosed vanadia–titania. Data is presented for samples with 6, 7, and 10 wt% vanadia.

studied. For comparison, the CH_2O desorption curve for pure TiO_2 is also included in this figure. Note that the high-temperature CH_2O peak for the 1 wt% vanadia sample is significantly more intense than that for the TiO_2 support, which occurs in the same temperature range. This demonstrates that for the supported vanadia catalysts, both the high- and low-temperature CH_2O desorption features are due primarily to reaction on the vanadia rather than the titania support. Thus, there are two separate reaction channels for the oxidation of surface methoxides to formaldehyde on the supported vanadia catalysts.

Thermal gravimetric analysis of the supported vanadia catalysts was also carried out during the CH_3OH TPD experiments. The number of adsorbed methoxy groups per surface vanadium cation is plotted as a function of sample temperature in Fig. 5 for the samples with 6 wt% and greater vanadia loadings. For the samples with lower vanadia loadings a significant fraction of the surface of the support is exposed; thus, the values for number of adsorbed methoxides per surface vanadium cation for these samples are not meaningful. Following methanol exposure at room temperature the number of methanols adsorbed per vanadium cation was 0.5, 0.32, and 0.21 for the samples with 6, 7, and 10 wt% vanadia, respectively. These values were relatively constant up to ~425 K and then decreased rapidly at higher temperatures. At 535 K, which is at the center of the low-temperature CH_2O desorption peak, the number of methoxides per vanadium cation was 0.34, 0.17, and 0.11 for the samples with 6, 7, and 10 wt% vanadia, respectively. The number of methoxides per surface vanadium cation for the 6 wt% sample is in agreement with that reported by Burcham and Wachs, who used FTIR to measure the methoxide concentration under steady state reaction conditions (29).

The effect of various catalyst pretreatments on reactivity was also studied using CH_3OH TPD. Although the pretreatment conditions influenced the peak shapes for all of the products, the most dramatic effect occurred for formaldehyde. Formaldehyde desorption curves obtained from a methanol-dosed 1 wt% vanadia sample for various pretreatment conditions are displayed in Fig. 6. Figure 6a was obtained from a fresh sample that had been briefly annealed at 500 K prior to the TPD experiment (this is the same curve as that for the 1 wt% sample in Fig. 2). As described above, the CH_2O desorption curve for this sample contained two overlapping peaks, centered at 535 and 630 K. Figure 6b was obtained in the subsequent CH_3OH TPD run with the same sample. Note that the CH_2O desorption curve now contains a single peak centered at 630 K. Figure 6c was obtained from a fresh sample that had been annealed in vacuum at 750 K prior to the TPD experiment. For this sample, CH_2O was again produced in two peaks, centered at 535 and 630 K. The relative size of the two peaks, however, varied significantly from

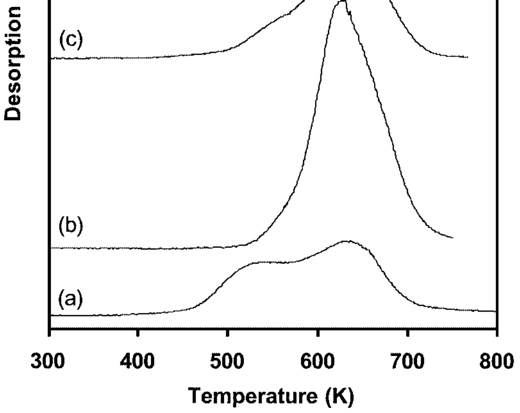

FIG. 6. Formaldehyde desorption spectra obtained from 1 wt% V_2O_5/TiO_2 during methanol TPD experiments for various sample pretreatments: (a) freshly prepared sample annealed at 500 K in vacuum prior to the TPD run; (b) subsequent TPD run with the sample used in spectrum a; (c) freshly prepared sample annealed at 750 K in vacuum prior to the TPD run; and (d) after reoxidation of the sample used in spectrum b in 0.1 Torr of O_2 at 475 K.

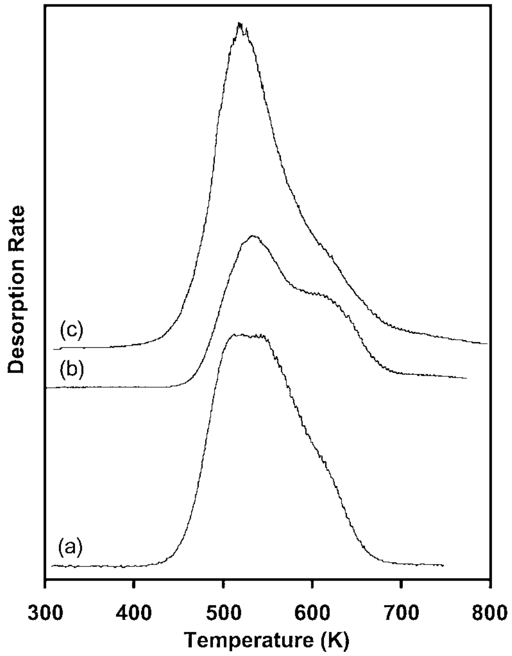

FIG. 7. Formaldehyde desorption spectra obtained from 7 wt% V_2O_5/TiO_2 during methanol TPD experiments for various sample pretreatments: (a) freshly prepared sample annealed at 500 K in vacuum prior to the TPD run; (b) subsequent TPD run with the sample used in spectrum a; and (c) after reoxidation of the sample used in spectrum b in 0.1 Torr of O_2 at 475 K.

that obtained for the sample annealed at only 500 K. The ratio of the area of the low-temperature peak to that of the high-temperature peak was 0.78 and 0.21 for the samples pretreated at 500 and 750 K, respectively.

It is possible that thermally induced reduction of the vanadia layer is responsible for the shift in the production of CH_2O to high temperature for the samples that had been either annealed at 750 K or subjected to a CH_3OH TPD run. In order to determine if this was indeed the case, the sample used for Fig. 6b was subjected to an oxidation treatment. This treatment consisted of exposing the sample to 0.1 Torr of O_2 and then heating to 475 K at a rate of 15 K/min. After the sample had cooled to room temperature the oxygen was evacuated and CH_3OH TPD experiment was performed. The CH_2O desorption spectrum obtained in this experiment is displayed in Fig. 6d. Note that after the oxidation treatment the low-temperature CH_2O peak remerges and is roughly twice as intense as the high-temperature peak.

A similar set of TPD experiments was performed for a 7 wt% sample. The CH_2O desorption curves obtained during CH_3OH TPD experiments with this sample as a function of pretreatment are displayed in Fig. 7. Figure 7a corresponds to a fresh sample that had been pretreated by annealing at 500 K. This spectrum contains a peak at 535 K with a broad tail to higher temperature. Figure 7b corresponds to the subsequent CH_3OH TPD run with the same sample. Two separate CH_2O desorption peaks can be resolved in this spectrum, centered at 535 and 630 K. The ratio of the area of the low-temperature peak to that at high temperate is 2.4. Figure 7c was obtained after oxidizing the sample used in Fig. 7b by exposing it to 0.1 Torr of O_2 while heating to 475 K at a rate of 15 K/min. This spectrum is similar to that for the fresh sample pretreated at 500 K and contains a large CH_2O peak at 535 K and a much smaller peak centered near 630 K.

The trends shown in Fig. 7 for the 7 wt% sample are similar to those in Fig. 6 for the 1 wt% sample. In both cases heating in vacuum or after exposing to CH_3OH produced a decrease in the ratio of the areas of low-temperature and high-temperature peaks, and exposure to oxygen produced an increase in this ratio. These results indicate that the extent of oxidation of the supported vanadia layer has a significant influence on the activation energy for the oxidation of adsorbed methoxides to formaldehyde. On highly oxidized supported vanadia this reaction proceeds at 535 K, while on partially reduced vanadia the reaction takes place at 630 K. As is discussed below, this conclusion is consistent with recent ultra-high vacuum studies of the reactivity of vanadia monolayers supported on single-crystal TiO_2 surfaces (15, 16).

Calorimetry

Calorimetry was used to measure the isosteric heat of reoxidation of the partially reduced supported vanadia catalysts. In this set of experiments each catalyst was initially reduced by annealing in 50 Torr of CH_3OH at 750 K. The isosteric heat of adsorption of oxygen at 425 K was then measured for a series of small O_2 pulses using the microcalorimeter. The isosteric heat per mole of O_2 adsorbed is plotted in Fig. 8 for samples with vanadia loadings of

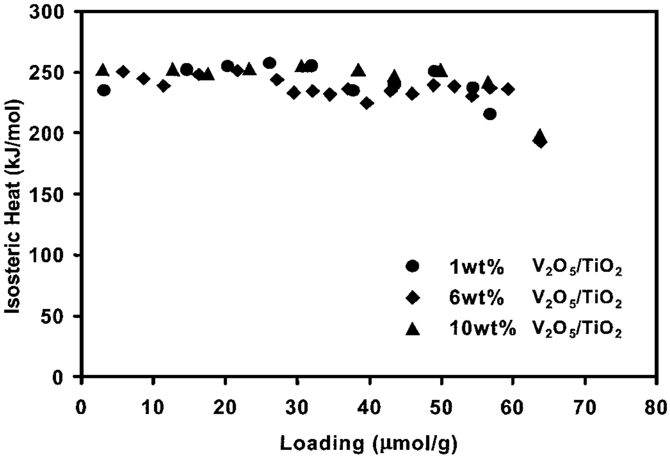

FIG. 8. The isosteric heat of adsorption of O_2 at 425 K for 1, 6, and 10 wt% V_2O_5/TiO_2. Each sample was reduced prior to the calorimetry measurements by annealing in 50 Torr of CH_3OH at 750 K.

1, 6, and 10 wt%. The measured heat of adsorption was 240 ± 10 kJ/mol of O_2 and was independent of the vanadia loading.

Additional calorimetry experiments were performed for a pure titania sample and a 20 wt% vanadia–titania catalyst. These samples were also initially annealed in 50 Torr of CH_3OH at 750 K. For both samples oxygen did not adsorb following this treatment, indicating that the samples had not been reduced. The lack of reduction of the pure titania allows the heat of adsorption measured for the vanadia–titania samples to be attributed to the interaction of oxygen with the supported vanadia layer and not with the surface of the support. Since 20 wt% vanadia is significantly higher than that required for monolayer coverage, this sample is composed of large vanadia crystallites supported on titania. The fact that annealing at 750 K in methanol was sufficient to partially reduce samples with 10 wt% or less vanadia but not the 20 wt% sample, therefore, demonstrates that the supported vanadia monolayers are much more reducible than bulk V_2O_5.

DISCUSSION

The TPD results clearly show that there are two separate reaction channels for the oxidation of surface methoxides to formaldehyde on vanadia supported on titania. During methanol TPD, formaldehyde is produced at both 535 and 630 K. The results of the TPD experiments as a function of the catalyst pretreatment conditions indicate that the low-temperature CH_2O peak is due to reaction on highly oxidized vanadia (i.e., V_2O_5), while the high-temperature peak is due to reaction on partially reduced vanadia. Recent ultra-high vacuum TPD studies of the reaction of methanol on model catalysts consisting of vanadia layers supported on single-crystal metal oxide surfaces (15, 16, 30, 31) provide additional evidence to support this conclusion. Wang and Madix studied V_2O_5 monolayers on $TiO_2(110)$ that were produced by adsorption and subsequent hydrolysis of $VOCl_3$ (15). During CH_3OH TPD on $V_2O_5/TiO_2(110)$, formaldehyde was the primary oxidation product and desorbed in a peak centered at 517 K. This peak temperature is close to that obtained in the present study for highly oxidized vanadia–titania catalysts. Wong *et al.* have studied the reactivity of V_2O_3 monolayers supported on $TiO_2(110)$ that were produced via vapor deposition of vanadium metal followed by annealing in O_2 (16, 30). Formaldehyde was also produced during methanol TPD experiments on $V_2O_3/TiO_2(110)$, but with a higher peak temperature of 610 K. Note that this peak temperature is only slightly lower than that of the high-temperature CH_2O peak from the high-surface-area vanadia–titania catalysts that had been previously annealed to 750 K. We have also recently used TPD to study the reaction of methanol on V_2O_5 and V_2O_3 monolayer films supported on $CeO_2(111)$ (31). The reactivity trends for the vanadia films on $CeO_2(111)$ were similar to those for vanadia supported on $TiO_2(110)$. For $V_2O_5/CeO_2(111)$, CH_2O was produced at 540 K during CH_3OH TPD, while for $V_2O_3/CeO_2(111)$ CH_2O was produced at 600 K.

The similarity in the TPD results for V_2O_5 and V_2O_3 supported on $TiO_2(110)$ and $CeO_2(111)$ allow the low- and high-temperature CH_2O peaks for the high-surface-area catalysts to be assigned to reaction on oxidized vanadium species that contain V^{+5} and V^{+3}, respectively. The temperature at which CH_2O is produced during methanol TPD can, therefore, be used as a chemical probe of the oxidation state of the supported vanadia layer. The correspondence between the CH_2O peak temperatures for vanadia supported on both high-surface-area titania and $TiO_2(110)$ demonstrates that for the high-surface-area samples, readsorption and diffusion do not significantly influence the TPD results. Thus, one can use the TPD data from the high-surface-area sample to estimate the activation energy for the reaction of methoxide to formaldehyde. Assuming first-order kinetics and a preexponential factor of 10^{13} s^{-1} the activation energies for the formaldehyde peaks at 535 and 630 K are estimated to be 150 and 177 kJ/mol, respectively.

In light of the dependence of the TPD results on the extent of reduction of the vanadia layer, it is useful to reexamine the data in Fig. 4 for the production of CH_2O during CH_3OH TPD as a function of the vanadia loading. As shown in this figure, for fresh samples that had been pretreated by annealing at 500 K, the ratio of the area of the low-temperature CH_2O peak to that at high temperature increased with an increase in vanadia loading. For the 10 wt% vanadia sample, only the low-temperature CH_2O peak was observed. This trend in the ratio of the areas of the low- and high-temperature CH_2O peaks can be attributed to an increase in the extent of reduction of the vanadia layer with a decrease in vanadia loading. Since the catalysts were calcined in air during synthesis and were initially in a highly oxidized state, reduction must have occurred upon heating to 500 K in vacuum. The data in Figs. 6 and 7 are consistent with this conclusion and show that the ratio of the areas of the low- and high-temperature CH_2O peaks increase significantly after treating a reduced sample in O_2 at 475 K. Thus, the thermal stability of the supported vanadia layer increases with an increase in vanadia coverage.

Differences in the structure of the supported vanadia at low and high loadings may be responsible for the dependence of the thermal stability of the supported vanadia layer on coverage. Raman studies indicate that at low coverage (<0.32 monolayer), vanadia forms isolated vanadyl complexes on TiO_2 and at higher coverages (0.32–1 monolayer) these species polymerize, producing polyvanadates (14). The TPD results obtained in this study suggest that the polyvanadate species may be more thermally stable than the isolated vanadyls. Based on these observations one might expect the heat of reoxidation of the partially reduced supported vanadia layer to also depend on coverage. This hypothesis, however, is not borne out by the calorimetry data presented in Fig. 8. The heat of reoxidation of the reduced vanadia layer was 240 ± 10 kJ/mol of O_2 and nearly independent of vanadia loading for loadings up to 10 wt%. It is possible that both isolated vanadyls and polyvanadate species are present on the surface of the samples with the higher vanadia loadings and that for all vanadia loadings studied the measured heats correspond to reoxidation of only vanadyl species. Additional calorimetry studies, in which more-stringent reduction treatments are used, such as annealing in H_2, are currently underway in order to test this hypothesis.

It is useful to compare the measured heat of reoxidation of the supported vanadia to values predicted by bulk thermodynamics. Heats of reaction at 425 K for the oxidation of V_2O_3 to V_2O_4 and V_2O_5 and the oxidation of V_2O_4 to V_2O_5 are as follows (32):

$$\begin{aligned} 2\,V_2O_3 + O_2 &\rightarrow 2\,V_2O_4, & \Delta H &= -379.72\ \text{kJ/mol of } O_2;\\ 2\,V_2O_4 + O_2 &\rightarrow 2\,V_2O_5, & \Delta H &= -306.24\ \text{kJ/mol of } O_2;\\ V_2O_3 + O_2 &\rightarrow V_2O_5, & \Delta H &= -342.98\ \text{kJ/mol of } O_2. \end{aligned}$$

Note that the ΔHs for all of these reactions are significantly greater than the ΔH for reoxidation of the supported vanadia monolayers, which was 240 ± 10 kJ/mol of O_2. These results show that bulk thermodynamics do not apply to the supported vanadia monolayers. The bonding energy of oxygen in the supported monolayers is significantly less than that in the bulk oxides. This observation is not particularly surprising in light of the lower coordination of the oxygen ions in a supported vanadia monolayer relative to that in the bulk oxides. The lower bonding energy of oxygen in the supported vanadia monolayers compared to the bulk oxides is also consistent with the monolayer species being a much more active oxidation catalyst. It would be interesting to compare the heats of reoxidation of vanadia monolayers on different oxide supports. Variations in the heat of reoxidation with changes in the identity of the support might provide considerable insight into the role of the support in influencing the reactivity of the vanadia. We are currently performing these measurements using our microcalorimeter and they will be reported in a future publication.

CONCLUSIONS

The results of this study demonstrate that methanol TPD is a very useful technique for the characterization of supported vanadia catalysts and provides a sensitive chemical probe of the extent of reduction of the vanadia layer. During TPD with methanol-dosed vanadia–titania samples formaldehyde was produced at two separate temperatures, 535 and 630 K, which can be attributed to dehydrogenation of methoxide species adsorbed on V^{+5} and V^{+3}, respectively. Based on these peak temperatures, the activation energy for methoxide dehydrogenation was estimated to be 150 kJ/mol on V^{+5} and 177 kJ/mol on V^{+3}.

Comparisons of CH_3OH TPD results obtained as a function of the sample pretreatment conditions demonstrated that the ease of reduction of the supported vanadia layer varied significantly with coverage. The reducibility of the supported vanadia decreased as the vanadia loading was increased from 1 to 10 wt%. Calorimetry studies showed that heat of reoxidation of supported vanadia that had been reduced by annealing in methanol was 240 ± 10 kJ/mol of O_2 and independent of the vanadia loading for weight loadings up to 10%. In contrast, annealing in methanol was insufficient to reduce a 20 wt% vanadia sample. These results in conjunction with comparisons to heats of reaction for the oxidation of V_2O_3 and V_2O_4 to V_2O_5 demonstrate that bulk thermodynamics cannot be used to describe supported vanadia monolayers. The bonding energy of oxygen in the supported monolayers is significantly less than that in the bulk oxides.

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