Mechanism of β-Hydrogen Abstraction from Adsorbed Alkoxides on Supported Metal Oxide Catalysts

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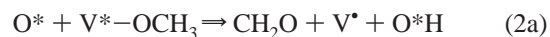*Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6393*

The transition state and the mechanism of β-hydrogen abstraction from alkoxides adsorbed on vanadia monolayers supported on both ceria and anatase titania were investigated using a combination of temperature-programmed desorption (TPD) and microcalorimetry. The TPD studies demonstrated that the peak temperature for β-hydrogen abstraction from adsorbed ethoxides to produce acetaldehyde increased as the methyl group in the ethoxide was fluorinated. The calorimetry results showed that methyl group fluorination did not affect the heat of dissociative adsorption of the ethanol reactant. These observations are consistent with a transition state in which there is a positive charge on the β-carbon in the ethoxide and indicates that the reaction proceeds via hydride transfer to a vanadium site.

Introduction

Vanadia and molybdena supported on a second metal oxide are both well-known selective oxidation catalysts. Important distinguishing characteristics of these catalysts include the fact that the active component (i.e., vanadia or molybdena) must be highly dispersed and present as a monolayer or submonolayer film in order to exhibit high activity, and that the reactivity is strongly dependent on the identity of the underlying metal oxide support.[1−8] This latter characteristic is commonly referred to as the support effect, and its mechanistic origin is not well understood. Raman studies of supported oxide catalysts indicate that the underlying support does not strongly influence the structure of the active oxide phase;[9−11] thus, the support effect does not appear to be structural in origin. Proposed explanations for the support effect include variations in the metal−oxygen bond strengths for the oxygens that bridge between the support and the vanadium or molybdenum cations[4] and support-induced variations in the density of electronic states on the cations in the supported oxide layer.[5,12]

The selective oxidation of methanol to formaldehyde has been used extensively as a prototypical reaction for characterizing the activity of supported oxide catalysts.[1,2,5,10,13,14] Spectroscopic studies show that methanol adsorbs dissociatively on the supported oxide, forming a methoxide intermediate which then undergoes β-C−H bond cleavage to form formaldehyde. (β is used here because the C−H bond is in a position β to the surface.) Isotopic labeling studies have demonstrated that hydrogen abstraction from the methoxide is the rate-limiting step for the overall reaction.[15−17] The remaining steps in the mechanism include the reaction of the abstracted hydrogens to form water and reoxidation of the supported oxide layer. Thus, the mechanism for the oxidation of methanol to formaldehyde on supported vanadia is often depicted as follows:[4,5]

$$CH_3OH + V^* + O^* \leftrightarrow V^*\text{-}OCH_3 + O^*{-}H \quad (1)$$

$$O^* + V^*{-}OCH_3 \rightleftharpoons CH_2O + V^\bullet + O^*H \quad (2a)$$

$$2O^*{-}H \leftrightarrow O^* + H_2O + \square \quad (3a)$$

$$O_2 + 2\square \leftrightarrow 2O^* \quad (4)$$

where $\square$, V*, O*, and V$^\bullet$ correspond to an oxygen vacancy, a fresh vanadia site, an oxygen site, and a reduced vanadia site, respectively. Note that reoxidation of the reduced vanadium site would accompany reaction 4. Reaction 2a is the rate-limiting step and as is commonly done in the literature,[14,18−22] it is written as a proton transfer to a basic oxygen site to produce an adsorbed hydroxyl group. There is at least some evidence in the literature that supports the assertion that this reaction proceeds in this manner. For example, Allison and Goddard have reported ab initio quantum chemical calculations for supported molybdena that indicate that the β-hydrogen is abstracted by a neighboring oxo site.[19] On the other hand, it has also been suggested that the rate-limiting step may occur via hydride transfer to a metal site[23] as shown below in reaction 2b.

$$V^*{-}OCH_3 \rightleftharpoons CH_2O + V^*{-}H \quad (2b)$$
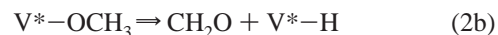
The metal-bound hydride formed in this manner would either rapidly transfer to an oxygen site or react with a neighboring hydroxyl group to produce water as shown in reaction 3b

$$V^*{-}H + O^*{-}H \leftrightarrow V^\bullet + H_2O + \square \quad (3b)$$
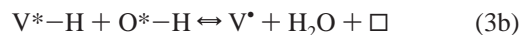
Weber has reported molecular orbital calculations for C−H bond cleavage in methoxide intermediates adsorbed on a series of vanadium-substituted Keggin ions that support the hydride transfer mechanism.[24] More recently, Oyama et al. have invoked the hydride transfer mechanism in a proposed explanation for the support effect.[5] In that study it was shown using near-edge

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X-ray adsorption fine structure spectroscopy (NEXAFS) data that the reactivity of a series of supported molybdena catalysts correlated with the density of unoccupied electronic states on the Mo cation, which was controlled in part via interactions of the molybdena with the support. It was argued that the variations in the density of unoccupied electronic states affected the preexponential factor for the transfer of a hydride from an adsorbed alkoxide to the metal center.

As the above discussion indicates, the details of the mechanism of the C−H bond cleavage reaction from alkoxides on supported oxides is important in understanding the factors that control the activity and selectivity of this class of catalysts. While the previous literature provides some clues as to whether this reaction proceeds via transfer of the hydrogen to an oxygen ion or to a metal cation, the detailed mechanism is still an open question. The goal of the study described here was to experimentally determine whether this reaction proceeds via proton or hydride transfer.

The experimental approach we have used to address this issue relies on the measurement of the activation energies for β-C−H bond cleavage from a series of fluorinated ethoxides adsorbed on a supported vanadia catalyst and is similar to that first used by Gellman et al. to study β-C−H bond cleavage from alkoxides adsorbed on Cu and Ag surfaces,[25−29] and later by Cong and Masel for similar reactions on Pt.[30] Gellman et al. used temperature-programmed desorption (TPD) to measure the kinetics of the dehydrogenation of ethoxide and fluorinated ethoxides to produce acetaldehyde and its fluorinated analogues and observed a systematic decrease in the rate of this reaction with increasing extent of fluorination on both Cu(111) and Ag-(110) surfaces.[25−29] The heats of adsorption of the alcohols on these surfaces were also determined from equilibrium adsorption data and found to be nearly independent of the extent of fluorination of the methyl group. On the basis of these results, it was concluded that fluorination causes an increase in the energy barrier for β-C−H bond cleavage in the alkoxide. Furthermore, Gellman et al. argued that the increase in the energy barrier resulted from an increase in the field effect of the methyl group upon addition of the electronegative fluorines and this in turn served to destabilize a polar transition state in which the β-carbon is cationic in character, i.e., $C^{\delta+}\cdots H^{\delta-}$. Recall that the substituent field effect is an empirical measure of how the electrostatic field of the substituent interacts with the charge or dipole that is present at the reaction site in the transition state. On the basis of these observations, it was concluded that at least on Cu and Ag surfaces β-C−H bond cleavage proceeds via hydride transfer to the surface rather than via proton transfer. In the present study, the kinetics of the oxidation of a series of fluorinated ethoxides to produce acetaldehyde or its fluorinated analogues on V_2O_5/TiO_2 and V_2O_5/CeO_2 were also measured using TPD. In contrast to the previous studies of Gellman et al.,[25−29] our measurements were made using high-surface-area polycrystalline samples as opposed to single crystals. The polycrystalline samples allowed a microcalorimeter to be used to directly measure the heats of dissociative adsorption of the alcohols.

Experimental Section

The catalysts used in this study consisted of 6 wt % vanadia supported on ceria and 7 wt % vanadia supported on anatase titania. Previous studies have shown that these vanadia loadings correspond to roughly monolayer coverage.[31,32] The anatase TiO_2 support was obtained from Degussa (Degussa P-25) and the CeO_2 support was synthesized by decomposing $Ce(NO_3)_3 \cdot$

$6H_2O$ (99.5% Alfa Aesar) in air at 875 K for 5 h. The surface areas of the TiO_2 and CeO_2 supports were 52 and 35 m^2/g, respectively, as measured by the BET method. The vanadia layers were deposited via the incipient-wetness method using an aqueous solution of ammonium metavanadate (NH_4VO_3, Sigma) and oxalic acid ($C_2O_4H_2$, Aldrich) in a 1:2 molar ratio. After impregnation of the vanadate, the samples were dried overnight at 400 K and then calcined in air at 775 K for 5 h.

The TPD apparatus used in this study has previously been described in detail[32] and consisted of a Cahn microbalance interfaced to a vacuum system equipped with a mass spectrometer (Thermo ONIX). For TPD studies, a 30−40 mg catalyst sample was loaded into the sample pan of the microbalance and the system was evacuated to a baseline pressure of 10^{-7} Torr. The hanging pan assembly of the microbalance was enclosed in a quartz glass thimble. The sample was heated using a tube furnace which was placed around the quartz glass thimble. After being placed into the TPD system, the supported-vanadia sample was pretreated by heating in 1 Torr O_2 at 775 K in order to clean the surface and guarantee that the vanadia layer was fully oxidized. For a TPD experiment, the catalyst was initially exposed to ∼15 Torr ethanol or fluorinated ethanol 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 the adsorbate 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 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. The alcohol reactants used in this study, CH_3CH_2OH (Aldrich, 99.5 +%), CF_2HCH_2OH (Avocado, 97%), and CF_3CH_2OH (Alfa Aesar, 99 +%) ,were purified using freeze−pump−thaw cycles prior to use.

One must be careful when using TPD to measure kinetics parameters from polycrystalline samples, since readsorption and diffusional limitations may affect the peak temperatures and shapes. This is especially true when the TPD experiment is performed at atmospheric pressure using a carrier gas that is swept over the catalyst. We have avoided these problems in the present study by using a vacuum TPD apparatus. We have previously used this system in TPD studies of the reaction of methanol on polycrystalline V_2O_5/TiO_2 and V_2O_5/CeO_2.[31,32] The primary reaction pathway for methanol is dehydrogenation to produce formaldehyde. The CH_2O desorption temperatures during TPD with methanol-dosed polycrystalline samples were found to be nearly identical to those obtained using single-crystal model systems consisting of vapor-deposited vanadia films supported on $TiO_2(110)$[33,34] and $CeO_2(111)$[17] single crystals in ultrahigh vacuum; thus, confirming that readsorption and diffusional limitations are not significant for our experimental setup.

Calorimetry was used to determine the heats of adsorption of ethanol and fluorinated ethanol on fully oxidized catalysts. A detailed description of the custom-built calorimeter used in this study can be found in previous papers.[31,35] Approximately 2 g of the catalyst was used in each calorimetry experiment. The sample was initially pretreated by annealing in 50 Torr oxygen at 775 K for 20 min. The heat of adsorption of each
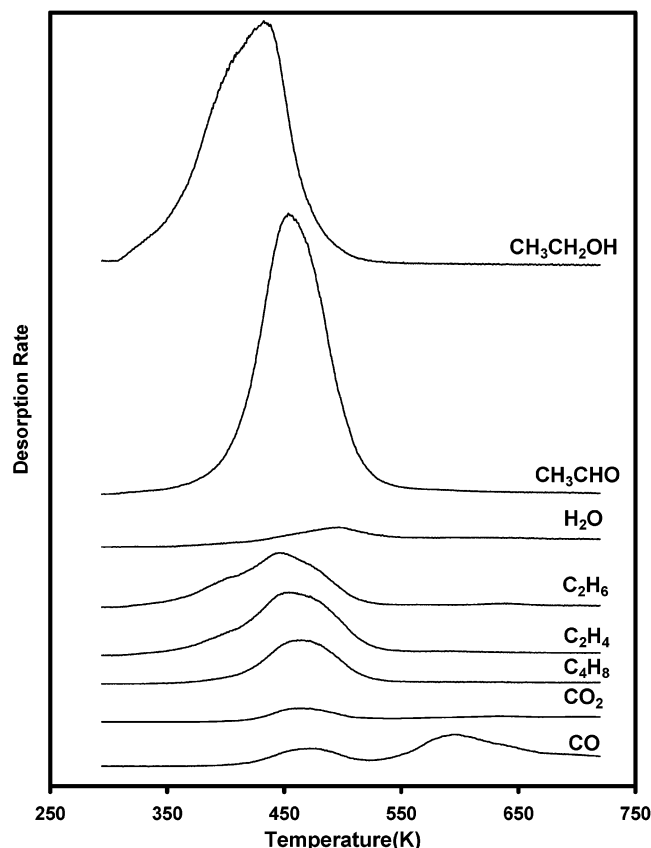
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Figure 1. TPD spectra obtained from CH_3CH_2OH-dosed 6 wt % V_2O_5 supported on ceria.

Figure 2. TPD spectra obtained from CF_3CH_2OH-dosed 6 wt % V_2O_5 supported on ceria.

alcohol was measured for a series of small pulses of the alcohol vapor with the sample held at room temperature.

Results and Discussion

TPD spectra obtained from a C_2H_5OH-dosed 6 wt % V_2O_5/CeO_2 sample are shown in Figure 1. The primary desorbing species were C_2H_5OH and CH_3CHO (acetaldehyde), which appeared in peaks centered at 435 and 455 K, respectively. Small amounts of the hydrocarbons C_2H_6, C_2H_4, and C_4H_8 were also produced near 460 K. The only other products detected were CO_2, which was produced at 460 K, and CO, which was produced at both 475 and 600 K. As expected, these TPD results are similar to those reported previously for the reaction of methanol on supported vanadia. Methanol adsorbs dissociatively at room temperature on supported V_2O_5 monolayers and forms methoxide intermediates.[36−39] The methoxide species undergo dehydrogenation upon heating to produce formaldehyde at near 530 K.[22,31,32] By analogy to the TPD results for methanol, one would expect ethanol to adsorb dissociatively on supported vanadia to form an ethoxide intermediate. IR studies have previously shown that this is indeed the case.[9] The ethanol peak in the TPD data in Figure 1 can therefore be attributed to recombinative desorption of an ethoxide and a proton from a surface hydroxyl group. Other ethoxide species remain on the surface to higher temperatures and undergo C−H bond cleavage at the *β* position to produce acetaldehyde at 455 K, which then rapidly desorbs. While the V_2O_5/CeO_2 catalyst is highly selective for the oxidation of ethoxide to acetaldehyde, the presence of small amounts of hydrocarbon products in the TPD spectra indicates that *γ*-C−H bond cleavage and C−O bond cleavage also occur to a small extent.

The temperature of the acetaldehyde peak in the TPD data from the ethanol-dosed sample depends on the energy barrier
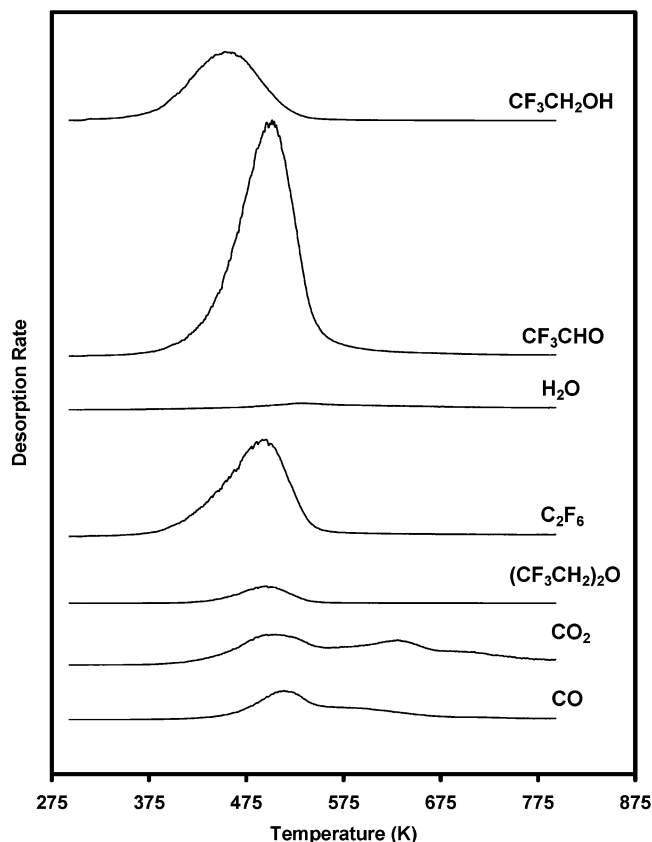
for the *β*-hydrogen elimination reaction. As described in the Introduction, the primary experimental goal of this study was to determine how this activation energy varies with fluorination of the methyl group on the ethoxide intermediate. Figure 2 displays TPD data obtained from a CF_3CH_2OH-dosed 6 wt % V_2O_5/CeO_2 sample. The TPD results for the 2,2,2-trifluoro-ethanol are similar to those obtained for ethanol in that the primary reaction pathway is *β*-hydrogen elimination from an adsorbed trifluoroethoxide to produce trifluoroacetaldehyde (CF_3CHO) at 490 K. Note, however, that this peak temperature is 35 K higher than that for the production of acetaldehyde from an adsorbed ethoxide. In addition to trifluoroacetaldehyde, the other products in the TPD spectra were CF_3CH_2OH at 460 K, which can be attributed to recombinative desorption of 2,2,2-trifluoroethoxide, and C_2F_6 at 495 K. As shown in the figure, small amounts of $(CF_3CH_2)_2O$, CO, and CO_2 were also produced between 400 and 700 K. In addition to the shift in the aldehyde peak temperature the primary difference between the TPD results for ethanol and 2,2,2-trifluoroethanol is the absence of alkene products when using the fluorinated reactant.

TPD spectra were also collected using 2,2-difluoroethanol as the reactant, and the results were similar to those obtained for CF_3CH_2OH and CH_3CH_2OH with *β*-hydrogen abstraction to produce CF_2HCHO at 475 K being the dominant reaction pathway. Figure 3 displays a comparison of the aldehyde desorption spectra obtained from CH_3CH_2OH-, CF_2HCH_2OH-, and CF_3CH_2OH-dosed 6 wt % V_2O_5/CeO_2 samples. Note that the aldehyde peak temperature increases with the extent of fluorination of the methyl group. The peak temperatures are 455, 475, and 490 K for CH_3CHO, CF_2HCHO, and CF_3CHO, respectively. While the influence of fluorination of the methyl group on the heat of dissociative adsorption of the alcohol and on the preexponential factor need to be considered, this result
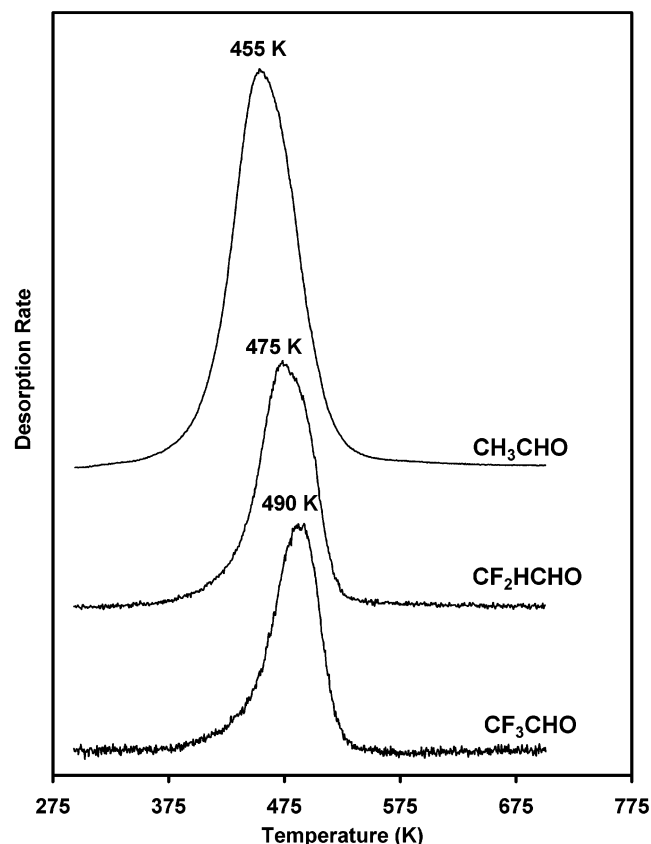
Figure 3. Aldehyde desorption spectra obtained during TPD from CH$_3$-CH$_2$OH-, CF$_2$HCH$_2$OH-, and CF$_3$CH$_2$OH-dosed 6 wt % V$_2$O$_5$ supported on ceria.

Figure 4. Aldehyde desorption spectra obtained during TPD from CH$_3$-CH$_2$OH-, CF$_2$HCH$_2$OH-, and CF$_3$CH$_2$OH-dosed 7 wt % V$_2$O$_5$ supported on titania.

suggests that the activation energy for C−H bond cleavage increases with the extent of fluorination. This result is similar to that reported by Gellman et al. for β-hydrogen abstraction from a series of fluorinated ethoxides to produce aldehydes on both on Cu(111) and Ag(110).[26−29]

To determine if the trend observed for the aldehyde desorption temperature with increasing fluorination is a general property of β-hydrogen abstraction reactions from alkoxides on supported vanadia or is specific to V$_2$O$_5$/CeO$_2$, a similar set of TPD experiments was performed for a 7 wt % V$_2$O$_5$/TiO$_2$ sample. For this sample, the primary reaction pathway was again dehydrogenation of adsorbed ethoxides to produce acetaldehyde or its fluorinated analogues. The aldehyde desorption spectra obtained in this set of experiments are displayed in Figure 4. Note that the results are nearly identical to those obtained from V$_2$O$_5$/CeO$_2$, with the aldehyde peak temperature increasing form 450 K for CH$_3$CHO to 475 K for CF$_2$HCHO and to 495 K for CF$_3$CHO. This result indicates that the trend of an increasing aldehyde peak temperature with increasing fluorination of the methyl group in the ethoxide is not support-dependent and is a general characteristic of β-hydrogen elimination from alkoxides on supported vanadia.

As noted above, the most obvious explanation for the increase in the aldehyde desorption temperature with increasing fluorination of the methyl group is an increase in the activation energy for the C−H bond cleavage. Assuming that this is the case, it is still not clear whether the increase is due to destabilization of the transition state or to stabilization of the adsorbed ethoxide intermediate. It is also possible that the peak shift is due to a change in the preexponential factor for the hydrogen abstraction reaction.
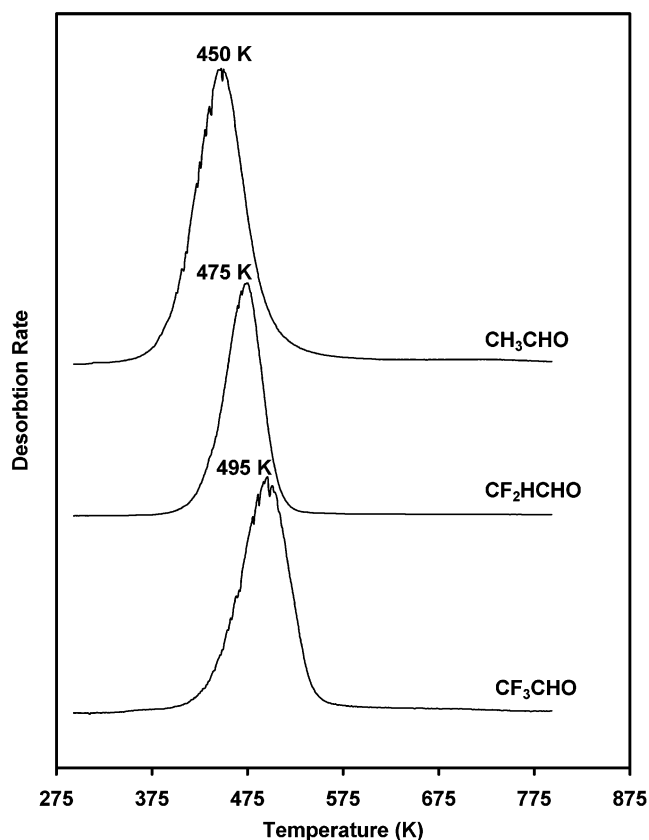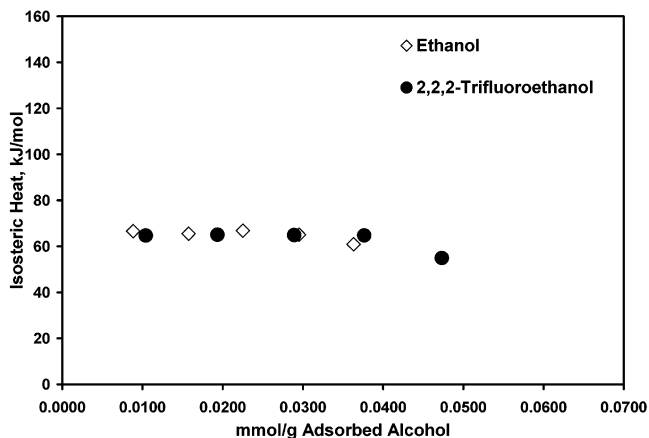

Figure 5. Heats of adsorption of CH$_3$CH$_2$OH and CF$_3$CH$_2$OH at room temperature on 6 wt % V$_2$O$_5$ supported on ceria.

To assess the effect of fluorination on the initial state, i.e., the depth of the energy well for the dissociative adsorption of the alcohol, microcalorimetry was used to measure the heats of adsorption of ethanol and 2,2,2-triflouroethanol as a function of the alcohol coverage at 300 K for a 6 wt % V$_2$O$_5$/CeO$_2$ sample. This calorimetry data is presented in Figure 5 and shows that for both species the heat of adsorption is 65 kJ/mol. Thus, fluorination of the methyl group has little if any effect on the heat of dissociative adsorption of the alcohols. This result is not particularly surprising and indicates that the methyl group in the adsorbed ethoxide does not interact strongly with the surface. A similar result has been reported by Gellman et al. for the heats of adsorption of ethanol and fluorinated ethanols on oxidized Cu(111).[25,26]

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The influence of fluorination of the methyl group in the adsorbed ethoxide on the preexponential factor for the C−H bond cleavage reaction is more difficult to ascertain. Ideally one would like to directly measure the preexponential factors when using ethanol and fluorinated ethanols as the reactants. For studies employing single crystals in an ultrahigh vacuum environment preexponential factors can be estimated by fitting a TPD spectrum to a first or second-order rate law.[40,41] This approach, however, is not appropriate for the present study which employed polycrystalline samples in a high-vacuum environment, since thermal gradients in the sample and the limited pumping speed of the vacuum system are likely to have caused some broadening of the desorption peaks. A more accurate method for determination of preexponential factors and activation energies requires the collection of TPD data as a function of heating rate.[40] For accurate estimates, however, this method requires that the heating rate be varied by at least an order of magnitude. Unfortunately, this again was not possible using polycrystalline samples and our experimental setup.

While the influence of fluorination of the methyl group in the ethoxide on the preexponential factor for the C−H bond cleavage reaction has not been measured, simple theoretical considerations can be used to predict the possible effect. According to transition state theory, the preexponential factor is proportional to the ratio of the partition function of the transition state to that of the reactant. (The partition function is a sum of Boltzman factors for all energy states of the molecule.) While fluorination of the methyl group would have a significant effect on both the vibrational and rotational energy levels, these effects would be similar for both the reactant (i.e., the adsorbed alkoxide) and the transition state and would therefore tend to cancel out. Thus, at least to a first approximation, transition state theory predicts that fluorination of the methyl group would have a relatively small effect on the preexponential factor. In their extensive TPD study of *β*-C−H bond cleavage from ethoxides on Cu(111), Gellman et al.[27] were able to determine preexponential factors by fitting individual desorption peaks and using peak temperature versus heating rate data. They found that the preexponential factor increased from $10^{15.2}$ s^{-1} for CH$_3$CH$_2$O− to $10^{17.9}$ s^{-1} for CF$_3$CH$_2$O−. On the basis of the theoretical arguments and the experimental results of Gellman et al., one would therefore predict that fluorination of the methyl group would at most cause a slight increase in the preexponential factor for C−H bond cleavage from the adsorbed ethoxides. Since an increase in the preexponential factor corresponds to an increase in the reaction rate, this would cause a decrease in the TPD peak temperature for the acetaldehyde product. Note that this trend is opposite to what was observed in the present study where the aldehyde peak temperature increased with increased fluorination. This leads to the conclusion that while changes in the preexponential factor may have a small affect, the changes in the acetaldehyde desorption temperature with extent of fluorination must be dominated by changes in the activation energy. Thus, the results of this study indicate that fluorination of the methyl group in an ethoxide adsorbed on a supported vanadia catalyst causes an increase in the activation energy for cleavage of the *β*-C−H bond.

While the preexponential factors have not been measured, the activation energies for the *β*-C−H bond cleavage from the ethoxides can be estimated using the TPD peak temperatures and assuming a standard preexponential factor of 10^{13} s^{-1}. These estimates for both the V$_2$O$_5$/CeO$_2$ and V$_2$O$_5$/TiO$_2$ samples are listed in Table 1. As shown in the table, for both V$_2$O$_5$/CeO$_2$ and V$_2$O$_5$/TiO$_2$ the activation energy increases by ∼10 kJ/mol
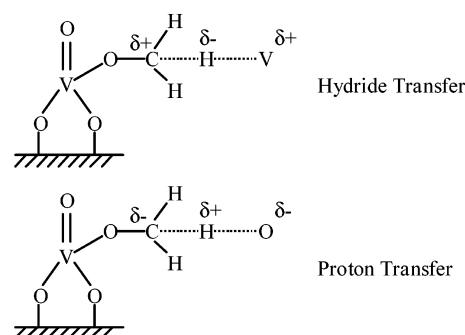

Figure 6. Schematic diagrams of possible transition states for *β*-hydrogen elimination from a methoxide intermediate.

TABLE 1: Activation Energies for *β*-Hydrogen Elimination from Alkoxides on CeO$_2$- and TiO$_2$-Supported V$_2$O$_5$ Catalysts

catalyst	alkoxide	T_p (K)	E_a (kJ/mol)
6 wt % V$_2$O$_5$/CeO$_2$	CH$_3$CH$_2$O	455	127
	CF$_2$HCH$_2$O	475	133
	CF$_3$CH$_2$O	490	137
7 wt % V$_2$O$_5$/TiO$_2$	CH$_3$CH$_2$O	450	125.5
	CF$_2$HCH$_2$O	475	133
	CF$_3$CH$_2$O	495	138.5

upon fluorination of the methyl group in the ethoxide. Note that the increase in the activation energy would be even larger if the preexponential factor also increased with fluorination as is the case for hydrogen abstraction from ethoxides on Cu-(111).[27] An increase in the preexponential factor by an order of magnitude upon fluorination would increase the difference in the activation energies between the ethoxide and trifluoro-ethoxide by 10 kJ/mol.

As described in the Introduction, there are two limiting cases for the mechanism of the *β*-hydrogen abstraction from the alkoxide: hydride transfer to the metal center and proton transfer to an oxygen ion. Schematic diagrams of the transition states for these two possibilities for a methoxide intermediate are displayed in Figure 6. Note that in the hydride-transfer case, the charge separation is such that the carbon atom in the methoxide has a net positive charge and is therefore cationic in character. In contrast, for the proton-transfer case, the carbon atom has a net negative charge and is anionic in character.

Simple energetics arguments similar to those presented by Gellman et al.[27,29] can be used to predict how fluorination of the methyl group in an adsorbed ethoxide would affect the stability of these two possible transition states. Due to the high electronegativity of fluorine, fluorination of the methyl group in the ethoxide increases the field substituent constant of the methyl group. This in turn would serve to stabilize a transition state in which there is a negative charge on the *β*-carbon as is the case for proton transfer. Thus, if the reaction proceeded via proton transfer, increasing the extent of fluorination of the methyl group would produce a decrease in the barrier for *β*-C−H bond cleavage. Just the opposite would occur in the case of hydride transfer where the increased field effect of the methyl group upon fluorination would destabilize a transition state in which there is a positive charge on the *β*-carbon and increase the barrier for *β*-C−H bond cleavage. The TPD and calorimetry results obtained in this study are consistent with this latter scenario and show that the energy barrier for *β*-C−H bond cleavage from adsorbed ethoxides increases with fluorination of the methyl group. The primary conclusion of this study, therefore, is that *β*-hydrogen elimination from adsorbed

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alkoxides on supported vanadia is best described as a hydride transfer reaction in which the hydride is transferred to the metal center.

Hydrogen elimination is ubiquitous in catalysis by supported metal oxides and occurs in the selective oxidation of alcohols to aldehydes or ketones and the oxidative dehydrogenation of alkanes to alkenes. While this study focused on the dehydrogenation of alkoxides on supported vanadia catalysts, it is likely that the results obtained in this study can be generalized to other supported oxide catalysts such as supported molybdena that exhibit similar reactivity trends. It is less clear, however, if the results obtained here can be applied to hydrogen elimination reactions from alkoxides on oxide surfaces in general. Obviously the local atomic structure of the surface and the accessibility of both cation and anion sites will strongly influence the mechanism of the reaction.

Conclusions

The TPD and calorimetry results obtained in this study show that the activation energy for the cleavage of the β-C−H bond in ethoxide intermediates adsorbed on vanadia monolayers supported on both ceria and titania systematically increases upon fluorination of the methyl group. This result is consistent with a transition state in which there is a partial positive charge on the β-carbon in the ethoxide and indicates that β-hydrogen elimination from adsorbed alkoxides on supported vanadia is best described as a hydride transfer reaction in which the hydride is transferred to the metal cation.

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