Surface Chemistry

Formaldehyde Formation on Vanadium Oxide Surfaces V₂O₃(0001) and V₂O₅(001): How does the Stable Methoxy Intermediate Form?**

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Dedicated to Professor Helmut Schwarz on the occasion of his 65th birthday

The oxidative dehydrogenation of methanol to formaldehyde ($CH_3OH + O \rightarrow CH_2O + H_2O$) is a frequently studied reaction of industrial importance. Herein we do not concentrate on the formaldehyde formation step itself (which will be discussed in forthcoming publications[1,2]) but rather try to shed some light onto the formation of the methoxy intermediate which precedes formaldehyde formation.[3] A methoxy layer forms on surface defects on V₂O₃(0001) and V₂O₅(001) even below room temperature through fission of the methanol O−H bond. This also produces hydrogen atoms that bind to the oxide surface and form hydroxy groups. Upon annealing, hydroxy groups may react to form water, consuming oxygen from the substrate. In turn this process may produce additional oxygen vacancies which act as reactive sites for methoxy formation. In addition to water formation, methanol formation through methoxy + hydroxy recombination may occur and compete with the water-formation reaction for

hydroxy groups. Their interplay determines the methoxy concentration at a given temperature. We discuss these processes for the example of methanol adsorption onto V₂O₃(0001) and V₂O₅(001). Both oxides were grown as thin layers on Au(111)[4,5] with layer thicknesses of 100 and 50 Å for V₂O₃(0001) and V₂O₅(001), respectively. Previous investigations[6–8] of vanadium oxide films on different substrates have shown that these are also active for formaldehyde production.

After preparation, both surfaces are terminated by a layer of vanadyl groups,[4,5] which inhibits methoxy formation. Removal of vanadyl oxygen atoms produces point defects which are reactive centers for methoxy formation[6] (for the surface structures see Figure 4 and the inset in Figure 5; the nature of point defects observed on V₂O₃(0001) is discussed in the Supporting Information). According to DFT calculations the energy for the formation of a single vanadyl oxygen vacancy with respect to $\frac{1}{2} O_2$ is 3.56 eV for V₂O₃(0001) and 1.84 eV for V₂O₅(001). The significantly smaller energy for V₂O₅(001) is the consequence of a lattice relaxation in which the reduced vanadium atom moves deeper into the surface and forms a bond to a vanadyl oxygen atom in the second layer.[9,10] A V^{3+}/V^{5+} pair is thus transformed into a V^{4+}/V^{4+} pair which reduces the vacancy formation energy. In the case of V₂O₃(0001) the bulk vanadium atoms are in a +3 oxidation state and therefore this stabilization process is not possible.

The high energy for the production of vanadyl oxygen vacancies prevents their preparation by thermal treatment for both oxide surfaces. Therefore electron irradiation was employed instead. The studies presented herein were performed using scanning tunneling microscopy (STM), temperature programmed desorption (TPD), infrared spectroscopy (IRAS), and density functional theory (DFT).

Figure 1 shows the density of methoxy groups and vanadyl oxygen vacancies on V₂O₃(0001) as a function of the degree of surface reduction by electron irradiation (dose Q). For the low electron doses employed in this case, the number of defects is proportional to the dose. This is also the case for the number of methoxy groups, but the gradient of the best-fit straight line is larger by a factor of two than that for the defects, demonstrating that one surface defect leads to two methoxy groups.

The intensity of the methoxy C−O vibrational infrared absorption band at approximately 1030–1040 cm⁻¹ increases by about a factor of two at 270 K (see Figure 2; a more

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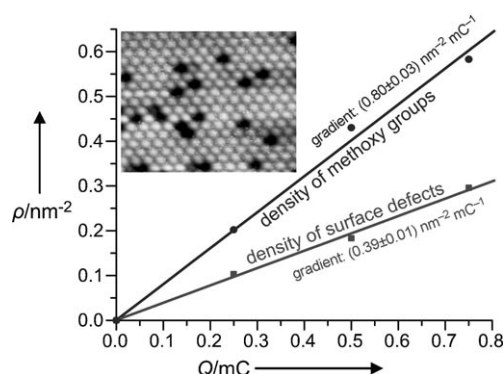Unter den Linden 6, 10099 Berlin (Germany)

Figure 1. Defect density as a function of the electron dose ($E_{kin} = 500$ eV) and the corresponding density of methoxy groups after methanol dosage at 90 K and a flash at 400 K (data obtained from STM images). Inset: STM image (7.0×5.7 nm) of vanadyl terminated $V_2O_3(0001)$ with some point defects.

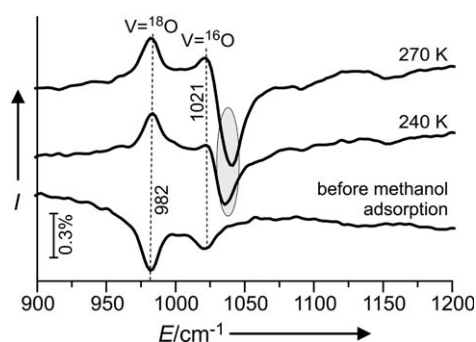**Figure 2.** Infrared spectra of methanol on weakly reduced $V_2O_3(0001)$ (containing ^{18}O and ^{16}O). Spectra were obtained after obtained after warming up to two different temperatures. Methanol was adsorbed at 90 K. For comparison, a spectrum of the surface recorded before methanol adsorption is shown. This spectrum is referenced to a spectrum of a surface without vanadyl oxygen atoms (vanadium terminated) and the other spectra are referenced to a spectrum recorded prior to methanol dosage.
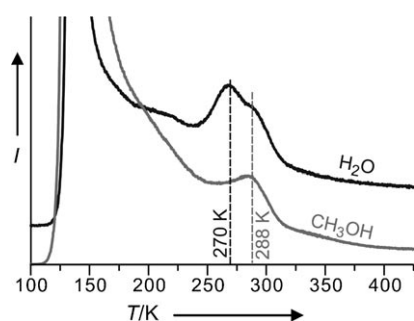

Figure 3. TPD traces (heating rate: 1 K s^{-1}; mass 18: H$_2$O and mass 31: CH$_3$OH) of methanol adsorbed at 90 K onto weakly reduced $V_2O_3(0001)$.

detailed discussion of the IR data is in the Supporting Information) and the TPD data (Figure 3) show that at 270 K water desorbs (the peak at 288 K in the mass 18 spectrum is a result of water formed from methanol by exchange reactions

at the walls in the mass spectrometer housing). These results indicate that only one methoxy group is formed per surface defect below 270 K and that the formation of the second methoxy group is connected with the production of water. Abu Haija et al. have shown that water formation from adsorbed hydroxy groups starts at 266 K[11] which is near to the 270 K observed in Figure 3.

The hydrogen atoms, originating from the formation of methoxy groups, bond to vanadyl oxygen atoms. This process reduces the density of surface vanadyl groups and gives rise to the positive intensities of the vanadyl vibrations in the upper two spectra in Figure 2. Water formation consumes the hydrogen atoms and some oxygen from the oxide support, that is, at 270 K a vanadyl oxygen atom leaves the surface as part of each water molecule formed. This produces additional defects which react with methanol to form more methoxy groups.

In step (1) of the surface reaction, methoxy and OH groups form when methanol is adsorbed at 90 K (reaction step (1)).

$$n\,CH_3OH + n\,V + n\,VO \rightarrow n\,CH_3OV + n\,VOH \qquad (1)$$
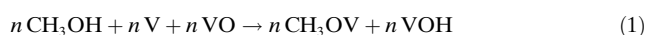
n is the initial number of surface defects V (vanadium sites). VO, CH$_3$OV, and VOH are vanadyl sites, methoxy and hydroxy groups, respectively. DFT results for a 2×2 cell with two defects yield an energy of 0.94 eV for the adsorption of one molecule of methanol per defect (Figure 4a). Additional
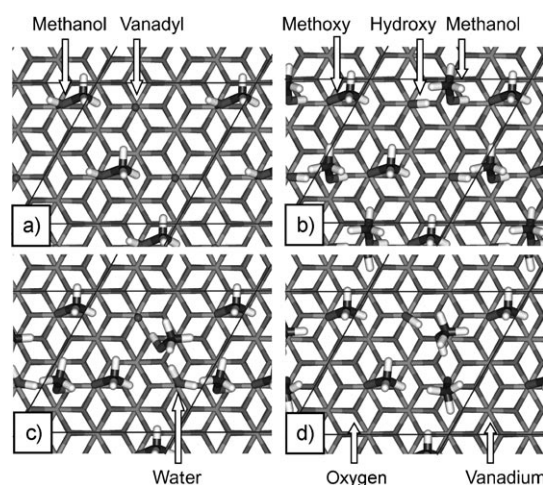

Figure 4. DFT results for the reaction of methanol on partially reduced $V_2O_3(0001)$ (2×2 cell).

methanol molecules can adsorb between the molecularly bound methanol molecules and adjacent vanadyl groups where they facilitate methanol dissociation to methoxy and hydroxy through a mediated transfer of hydrogen atoms (Figure 4b). The energy for dissociative adsorption is 2.00 eV per molecule and the additional bridging methanol molecules bind with an energy of 0.58 eV. After methanol dissociation, bridging methanol molecules may move towards a position

between two hydroxy groups where they mediate water formation by transfer of hydrogen once more (reaction step (2), Figure 4c).

$$n\,VOH \rightarrow \frac{n}{2}\,H_2O + \frac{n}{2}\,VO + \frac{n}{2}\,V \tag{2}$$

The water molecules are then displaced by bridging methanol molecules. Other bridging methanol molecules mediate the dissociation of the methanol molecules at the pristine water-adsorption site into methoxy and hydrogen (reaction step (3), Figure 4d) through transfer of the hydrogen atoms to the vanadyl groups formed in reaction step (2). Hereby the water molecules formed in reaction step (2) desorb.

$$\frac{n}{2}\,CH_3OH + \frac{n}{2}\,V + \frac{n}{2}\,VO \rightarrow \frac{n}{2}\,CH_3OV + \frac{n}{2}\,VOH \tag{3}$$
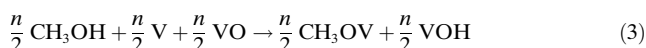
The calculated water desorption energy (energy difference between the structures in Figure 4b and 4d (including desorbed water) is 0.69 eV which is in good agreement with the experimental value of 0.74 eV calculated using Redhead's equation[12] for a water desorption temperature of 270 K. The desorption energy of a methanol molecule from the structure shown in Figure 4c is higher (0.93 eV), which means that methanol is still available at the temperature at which the hydroxy groups react. This situation is a requirement for the reaction in step (3) [Eq. (3)]. The hydroxy groups produced in this step again combine to form water and defects and the defects react with methanol to form more methoxy, and so on. This self-limiting chain reaction goes on until the number of produced defect sites approaches zero. The total number of methoxy groups finally formed is given by Equation (4) .

$$n\,CH_3OV + \frac{n}{2}\,CH_3OV + \frac{n}{4}\,CH_3OV + \ldots = 2n\,CH_3OV \tag{4}$$

Thus the number of methoxy groups is twice as large as the number of surface defects which is in full agreement with the data displayed in Figure 1. We note that this reaction also proceeds at room temperature and above if the dosing time is not too short.[1]

In the case of V$_2$O$_5$(001) a slightly different mechanism is operative in that not the formation of additional defects but the abundance of hydroxy groups is the critical parameter. Figure 5 shows that the methoxy coverage at room temperature (measured by the integrated intensity of mass 29 TPD spectra) depends in an unusual way on the methanol dose: even at low doses a high methoxy coverage is established which increases only slowly for higher doses. XPS and TPD data (not shown) show a decrease in the methoxy coverage together with methanol desorption between 230 and 280 K, which means that methoxy groups and hydrogen atoms recombine to form methanol in this temperature range (such a recombination reaction together with water formation was also assumed to occur on oxygen covered Cu(110)[13]). However, there seems to be a factor which limits the recombination reaction since there is methoxy on the surface at room temperature and the amount of methoxy even increases with increasing dose (Figure 5).
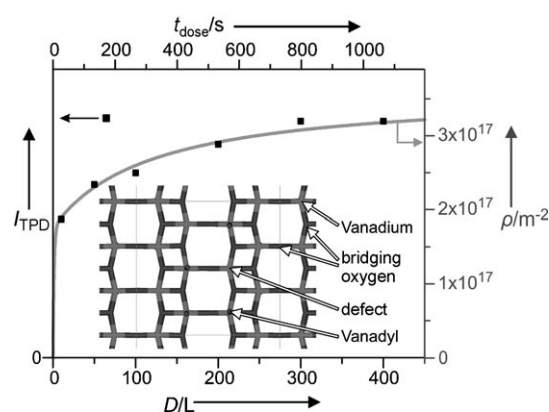

Figure 5. Density of methoxy groups on slightly reduced V$_2$O$_5$(001) (electron dose for reduction: 1 mC) as obtained from a quantitative evaluation of TPD data (■ values for peak area; for details see the Supporting Information) in comparison with the result of a kinetic simulation (solid line). The data are plotted as a function of the methanol dose at room temperature (bottom scale) and the dosing time (top scale). In the inset a model of a V$_2$O$_5$(001) surface with some vanadyl oxygen vacancies is shown.

In this case water formation is again the critical parameter. Methanol formation through the reaction of methoxy with hydroxy can only occur if hydroxy groups are available. If some of the hydroxy groups are removed due to water formation this will limit the methanol formation. To support this assumption we have developed a kinetic model for the methoxy and hydroxy surface coverages [Eq. (5) and (6)].

$$\frac{d\Theta_M}{dt} = S(\Theta_M)\Phi_M - \Theta_M\Theta_{OH}\nu_M e^{-E_M/kT} \tag{5}$$

$$\frac{d\Theta_M}{dt} = \underbrace{S(\Theta_M)\Phi_M}_{adsorption} - \underbrace{\Theta_M\Theta_{OH}\nu_M e^{-E_M/kT}}_{methanol formation} - \underbrace{2\Theta_{OH}^2\nu_{OH}e^{-E_{OH}/kT}}_{water formation} \tag{6}$$

Θ_M and Θ_{OH} are the time-dependent surface densities of methoxy and hydroxy group. $S(\Theta_M) = R - \Theta_M/N_{tot}$ is a coverage-dependent sticking coefficient, which is set to be proportional to the density of unoccupied adsorption sites with $N_{tot} = 4.8 \times 10^{18}$ m^{-2} the density of vanadyl sites and $R = 0.075$ the degree of reduction as determined by STM. We note that the choice of the sticking coefficient is not very critical as long as the adsorption rate is high enough to maintain a nearly complete surface coverage. $\Phi_M = 1.35 \times 10^{18}$ m^{-2}s^{-1} is the methanol flux onto the surface (which corresponds to 0.38 Ls^{-1}). The terms ν_M, ν_{OH}, E_M, E_{OH} are fit parameters and represent the frequency factors and the activation energies for methanol and water formation, respectively. k, t, and T are the Boltzmann constant, time, and temperature (298 K).

In the first step of the calculations the starting coverages were set to zero and the surface was exposed to the methanol flux given above until the intended dose was reached. Then the methanol flux was set to zero and the calculations were performed until a negligible hydroxy coverage was reached as a result of methanol and water formation and the reaction stopped.

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The best fit to the experimental data (solid line in Figure 5) gives $\nu_M = \nu_{OH} = 2.1 \times 10^{-6}\,m^2\,s^{-1}$ and $E_M = E_{OH} = 0.85\,eV$. The initial steep increase in coverage is due to the occupation of free sites with methoxy groups. The subsequent slow increase is due to methoxy formation on sites freed by methanol desorption with the hydrogen atoms contributing to water formation. This process ultimately leads to a surface on which all the defect sites are covered by methoxy groups that cannot undergo desorption because of the lack of hydrogen. Also in this case the water desorption leads to consumption of surface oxygen which was not considered in the model. According to STM (not shown here) the defects from water desorption form pairs perpendicular to the vanadyl double rows and are probably not active, or less active, for methoxy formation.

According to DFT calculations the energies for molecular and dissociative methanol adsorption onto a vanadyl oxygen vacancy on $V_2O_5(001)$ are 0.64 and 0.67 eV, respectively. For water, dissociative adsorption (0.43 eV) is less favored than molecular adsorption (0.64 eV; see also Hermann et al.[14] who discussed the case of oxygen-vacancy formation as well as water and OH desorption from $V_2O_5(0001)$). Thus, immediately after methanol dissociation, the resulting hydroxy groups would react to form water. As a result, no hydroxy groups would be left to produce methanol by reaction with methoxy. However, according to experiment results, methanol does form which shows that water formation must be hindered. This may be a consequence of an energy barrier which could also explain why the experimental activation energies (0.85 eV) for methanol and water desorption do not fit well to the calculated energy differences between the molecular and the dissociated states. The fact that the experimental activation energies and frequency factors for water and methanol formation are identical may indicate that the rate-limiting step is the same for both reactions. In view of the low adsorbate density, this step could be hydroxy diffusion on the surface which plays a role for both reactions and could limit their rate if the activation energy is high.

In summary, we analyzed in detail the mechanism of the formation of methoxy layers after methanol adsorption onto slightly defective $V_2O_3(0001)$ and $V_2O_5(001)$, highlighting the role of hydroxy groups resulting from the fission of methanol into methoxy and hydrogen. For $V_2O_3(0001)$, water formation from the reaction of two hydroxy groups produces additional defects which act as reactive centers for methanol dissociation thereby effectively doubling the methoxy coverage. For $V_2O_5(001)$ the reactions for methanol formation and water formation from surface hydroxy and methoxy groups compete for the hydroxy groups that stabilize the surface methoxy groups by production of a hydrogen deficiency. On the basis of DFT calculations a mechanism for methanol-assisted hydrogen transfer on $V_2O_3(0001)$ can be proposed which is operative for water formation from hydroxy groups as well as for dissociative methanol adsorption. We believe that the mechanisms discussed herein are of general importance for reactive methanol adsorption on oxide surfaces.

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