

Coupling Reactions in Aldehydes Adsorbed on V(100) Single-Crystal Surfaces

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Abstract: The thermal chemistry of formaldehyde on vanadium (100) single-crystal surfaces was characterized under ultrahigh vacuum (UHV) conditions by using temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) in combination with isotope-labeling experiments. Particular emphasis was placed on establishing a mechanism for the formation of ethylene, which was observed to desorb in two temperature regimes, at 290 and 540 K. The low-temperature reaction was determined to occur via the coupling of methylene groups formed on the surface upon dissociation of the C–O bond in adsorbed formaldehyde. The high-temperature ethylene, on the other hand, was proven to require the prior formation of a diolate, $-\text{OCH}_2\text{CH}_2\text{O}-$, intermediate. This chemistry was shown to be quite general, also occurring in cross-coupling mode between two different coadsorbed aldehydes.

1. Introduction

Reductive coupling of carbonyl species has proven a versatile strategy for the functionalization of vicinal carbon atoms in organic molecules.^{1,2} Coupling of aldehydes in particular was first reported by McMurry using titanium-based complexes,³ and low-valent vanadium compounds have been shown to effectively catalyze processes by which different kinds of aldehydes can be transformed to their corresponding dimerization products.^{4,5} The coupling mechanism usually involves the formation of carbonyl intermediates chelated to metal centers followed by a carbon–carbon bond formation step to generate a diolate intermediate.⁵ This reaction has typically been performed in homogeneous solutions, but it has also been observed in surface-science studies with oxides.^{6,7} A common feature of both types of systems, involving either organometallic complexes or the surfaces of oxides, is the participation of an early transition metal capable of undergoing redox chemistry. Here, we report surface-science studies indicating the ability of aldehydes adsorbed on vanadium metal surfaces to couple via a similar mechanism to yield a diolate-formation intermediate, and ultimately ethylene.

The adsorption and thermal conversion of aldehydes have already been investigated on a number of metal^{8–17} and metal

oxide^{6,7,13,16,18–21} surfaces, mostly on surfaces involving late transition metals. In general, the most common observation in these systems has been the decomposition of formaldehyde to carbon monoxide and hydrogen. In addition, decarbonylation of higher aldehydes to shorter-chain olefins has been reported in a number of occasions,^{13,16} and oligomerization and polymer formation have also been seen on a couple of metal surfaces.^{10,11,17,22} More relevant to this study, the coupling of aldehydes to alkenes has been identified on titanium⁶ and uranium oxides²³ surfaces, and also on Mo(110).⁹ Both methylene coupling after formaldehyde decomposition and prior coupling to a dimer intermediate following by ejection of the olefin have been considered.

In this paper we report on the key results from our studies on the thermal conversion of formaldehyde on V(100) single-crystal surfaces using temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) in combination with isotope-labeling experiments. Coupling of the aldehyde to produce ethylene was found to occur in two distinct temperature regimes, around 290 and 540 K, respectively. Particularly interesting is the chemistry involved in the second regime, where isotope-labeling experiments unambiguously point to an early carbon–carbon bond formation between adsorbed carbonyl intermediates, a step that is then followed by the scission of the C–O bonds to generate the corresponding

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olefin. Corroborative data suggest that the precursor that forms prior to the C–O scissions most likely adopts a diolate structure, as in vanadium-based catalysis with organometallic compounds.⁴ The diolate formation mechanism appears to be general, and was seen here with acetaldehyde and also in cross-coupling chemistry between formaldehyde and acetaldehyde.

2. Experimental Section

All the experiments reported here were conducted in an ultrahigh-vacuum (UHV) chamber evacuated with a turbo-molecular pump to a base pressure of about 2×10^{-10} Torr. A detailed description of this system can be found elsewhere.^{24,25} Briefly, the chamber is equipped with instrumentation for thermal programmed desorption (TPD), X-ray photoelectron (XPS), ion scattering (ISS), secondary ion mass (SIMS), and Auger electron (AES) spectroscopies. The TPD data were acquired by simultaneously recording the time evolution of the partial pressures of up to 15 masses in one run by using an Extrel quadrupole mass spectrometer. The ionizer of the mass spectrometer is located inside an enclosed compartment with a frontal aperture 7 mm in diameter, which is used for gas sampling during the TPD data acquisition. A linear heating rate of 10 K/s was employed, as set by a homemade temperature controller. The TPD signals are reported in arbitrary units, but intensity bars are provided in each plot for relative comparisons. The XPS spectra were acquired by using a 50-mm hemispherical electron energy analyzer and an aluminum-anode X-ray source. The pass energy was set at 50 eV for all measurements, and the energy scale was referenced to a value of 932.7 eV for the binding energy of the Cu $2p_{3/2}$ electrons.²⁶

The V(100) single crystal (99.99% purity, Goodfellow Cambridge Limited, ~12 mm in diameter and ~2 mm in thickness) was cut and polished using standard procedures, and spot-welded to two tantalum rods attached to an on-axis manipulator capable of rotation and translation in all three dimensions. The crystal could be cooled down to liquid-nitrogen temperatures and resistively heated to above 1300 K. The temperature was measured by a chromel-alumel thermocouple spot-welded to the back of the crystal. The V(100) surface was cleaned following a procedure described in detail in former publications,^{27–30} involving numerous sputtering and annealing cycles until no sulfur, carbon, or phosphor could be detected within the sensitivity of our instruments. A small amount of oxygen was inevitable on the annealed surface, but could be kept to reasonably low levels, and, according to tests in controlled experiments, appears to not seriously affect the results reported here.²⁹

Because of the extensive overlap of the cracking patterns of the mass spectra of the molecules in this study, a brief discussion of the procedure followed to analyze the TPD data is warranted. In general, a procedure commonly used in our group was employed here where the relative intensities of the TPD signals of a number of carefully selected masses are compared to those obtained in mass spectra of the relevant compounds and deconvoluted using a matrix analysis.³¹ In this case, the identification of normal formaldehyde was accomplished by using the TPD traces for 29 and 30 amu, of perdeuterioformaldehyde by using the data for 29, 30, and 31 amu

(the latter being unique to this species in most experiments), and of normal ethylene by using those for 26 and 27 amu. The cracking patterns of deuterated ethylenes needed for this deconvolution procedure were also available,^{32,33} as they have been measured with our instrument in the past.^{34–38} Deconvolution of the data in the isotope-labeling experiments was simplified by the high masses of the molecular ions of highly deuterated compounds, which could be used to uniquely follow their chemistry; subtraction of the signals from those to the TPD traces from products with less deuterium substitutions could then be carried out sequentially until reaching the nonlabeled molecules. The TPD traces from carbon monoxide were obtained using the raw data for 28 amu after subtraction of all other contributions, and corroborated by the (much weaker) traces seen for 12 and 16 amu. Confidence in our analysis was added by a number of observations across experiments, including: (1) the different positions and shapes ultimately obtained for each species, (2) the trends observed in the TPD results as a function of initial coverages (which are often different for different species), and (3) the consistency among results using different isotope labeling (or the different trends seen for each isotopomer in experiments such as those in Figure 3). Analysis of TPD data from similar systems has in fact been reported before.^{30,39}

Paraformaldehyde (95%), paraformaldehyde- d_2 (99%), acetaldehyde (>99%), ethylene glycol ($\geq 99\%$), and diiodomethane (99+ %), were all purchased from Aldrich, and acetaldehyde- d_4 (99%) was acquired from Cambridge Isotope Laboratory, Inc. The first two chemicals are solid and were heated to above 335 K to produce formaldehyde in the gas phase, while all liquid chemicals were purified via repeated freeze–pump–thaw cycles prior to use. All these gases were dosed by direct backfilling of the chamber via leak valves, and their purities frequently checked in situ by using the mass spectrometer available in the UHV chamber. O_2 (99.99%) was purchased from Matheson, and used as supplied. Gas doses are reported in langmuirs ($1 L = 10^{-6}$ Torr·s), uncorrected for differences in ion gauge sensitivities.

3. Results

Figure 1 summarizes the main results from TPD experiments with formaldehyde on clean V(100) single-crystal surfaces. The left panel shows the traces acquired for the main products that form upon thermal activation of 2.0 L of adsorbed formaldehyde on the V(100). As previously seen with methanol on the same surface,³⁰ the main desorbing products are carbon monoxide (550 K) and hydrogen (325 and 565 K), the result of complete formaldehyde dehydrogenation, methane (355 and 540 K) from hydrogenation of the methylene moieties in HCHO, and ethylene (290 and 540 K). Also to notice is the fact that the desorption of both methane and ethylene takes place within two temperature regions. The right panel of Figure 1 displays the traces for the formation of ethylene, the focus of our discussion below, as a function of initial formaldehyde exposure. Other products, including paraformaldehyde,¹⁰ acetic acid, and propene, were searched for but not detected.

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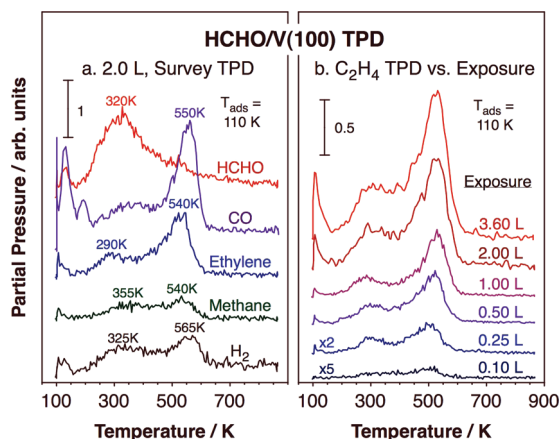


Figure 1. Temperature-programmed desorption (TPD) spectra for HCHO adsorbed on a clean V(100) surface at 110 K. Left panel: survey traces obtained after a 2.0 L dose showing the production of hydrogen, methane, ethylene, carbon monoxide, and molecular formaldehyde. Right panel: traces for ethylene production obtained after several increasing doses of formaldehyde. Heating rates of 10 K/s were used in these and all the other TPD experiments in this paper.

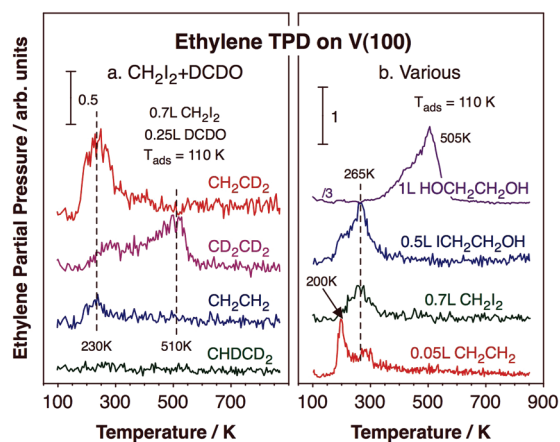


Figure 2. TPD spectra for ethylene production from V(100) surfaces dosed with different combinations of adsorbates. Left panel: CH₂CD₂, CH₂CH₂, and CD₂CD₂ TPD traces obtained after sequentially coadsorbing 0.25 L of DCDO and 0.7 L of CH₂I₂. The cross-coupling product, CH₂CD₂, is only observed at low temperatures. Right panel: comparison of ethylene TPD traces obtained with several different compounds: ethylene, diiodomethane, 2-iodoethanol, and ethylene glycol.

Figure 2 provides more information on the origin of the ethylene generated by the thermal activation of formaldehyde on V(100). Based on our previous results indicating that surface methylene groups on V(100) surfaces, prepared via thermal activation of diiodomethane, undergo low-temperature self-coupling to generate ethylene,⁴⁰ a test was performed to explore the possibility of methylene surface formation from formaldehyde by coadsorbing diiodomethane with perdeuterioformaldehyde. The isotope labeling allows for the tracking of the origin of each methylene moiety in the resulting ethylene: the formation of cross-labeled CH₂CD₂ provides a clear indication of coupling between methylene groups from diiodomethane and formaldehyde. The data in Figure 2a indicates that cross coupling indeed occurs at low temperatures, but not in the ethylene desorption peak above 500 K. Nonisotope-scrambled CH₂CH₂ and CD₂CD₂ are also produced below 300 K, as also seen with the individual CH₂I₂ (Figure 2b, second-from-bottom trace)⁴⁰ and DCDO

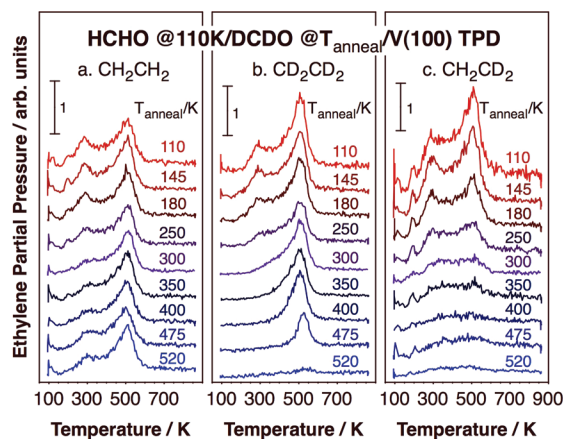


Figure 3. CH₂CH₂ (a), CD₂CD₂ (b), and CH₂CD₂ (c) TPD traces obtained after sequential coadsorption of DCDO and HCHO as a function of DCDO annealing temperature (the HCHO was always adsorbed at 110 K). The experimental protocol used is described in more detail in the text. Annealing the adsorbed DCDO to temperatures above 250 K leads to a dramatic decrease in CH₂CD₂ desorption yield.

molecules, respectively, and CD₂CD₂ is produced above 500 K as well, as in Figure 1. The low-temperature ethylene peak is therefore most likely the result of coupling of two methylene surface moieties, made from either diiodomethane or formaldehyde decomposition. On the other hand, the absence of ethylene with any normal hydrogen content at high temperatures proves that it is produced by a conversion involving only formaldehyde, and strongly suggests that it does not go through the formation of a methylene surface intermediate. Also, the lack of CHDCD₂ formation at any temperature rules out the participation of vinyl intermediates in the reactions with formaldehyde, as previously seen with diiodomethane.⁴⁰

Figure 2b shows reference ethylene desorption data acquired with different adsorbates on V(100). It is clear from those results that both diiodomethane and 2-iodoethanol can produce ethylene below 300 K. The data from 2-iodoethanol (Figure 2b, second-from-top trace) in particular suggest that the low-temperature ethylene desorption observed from the formaldehyde plus diiodomethane mixed layer may be generated via the formation of a -OCH₂CH₂I- intermediate rather than by coupling of two methylene adsorbates. However, it was seen that increasing the CH₂I₂ exposures used after DCDO deposition in the coadsorbed system leads to an enhancement in CH₂CD₂ yield (data not shown), a result that argues against the formation of any stoichiometric intermediates. The lower desorption temperature seen for ethylene molecular desorption (Figure 2b, lower trace) indicates that the chemistry seen in the TPD with the other compounds is all reaction- rather than desorption-limited.

As stated above, the production of ethylene from formaldehyde at ~500 K does not come from coupling of surface methylene groups, and most likely requires the formation of a different stable intermediate. To further test the origin of this ethylene precursor, TPD spectra were acquired from mixed-isotope layers made out of HCHO and DCDO where the perdeuterioformaldehyde was dosed first and annealed to different temperatures before adding the normal formaldehyde. The idea behind these experiments was to first activate the DCDO to determine at which stage it forms the intermediate responsible for the high-temperature ethylene and no longer yields the methylene species that can couple with additional (normal) formaldehyde. Figure 3 shows the resulting CH₂CH₂ (a), CD₂CD₂ (b) and CH₂CD₂ (c) TPD spectra obtained as a function

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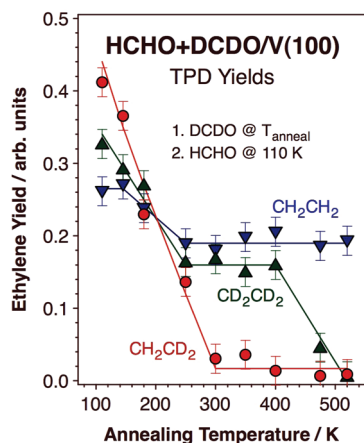


Figure 4. Summary of desorption yields calculated from the TPD traces reported in Figure 3. Two key observations from these experiments are highlighted here: (1) the significant decrease in CH_2CD_2 yield after annealing the initial DCDO to temperatures above 250 K and (2) the steady yield seen for CD_2CD_2 between 250 and 400 K. These results strongly suggest the formation of a stable dimeric intermediate before high-temperature ethylene production.

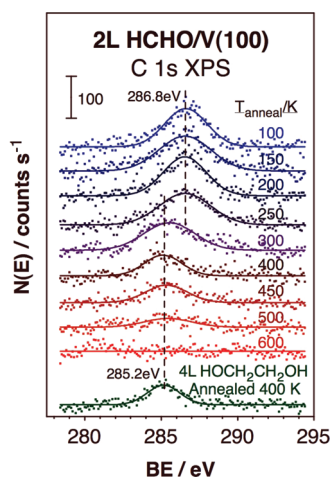


Figure 5. C 1s XPS spectra for formaldehyde adsorbed on a clean V(100) surface as a function of annealing temperature. A clear shift in peak position is observed between 250 and 300 K, from 286.8 to 285.2 eV. The latter position matches that obtained after annealing adsorbed ethylene glycol to similar temperatures (bottom trace), suggesting a similar surface species in both cases, namely, a diolate, $-\text{OCH}_2\text{CH}_2\text{O}-$.

of DCDO annealing temperature, and Figure 4 summarizes the yields obtained. It can be seen from these data that after using low annealing temperatures for DCDO a substantial amount of CH_2CD_2 is generated, close to that expected on the basis of a statistical analysis assuming similar coupling possibilities between CH_2 and CD_2 , CH_2 and CH_2 , and CD_2 and CD_2 . After annealing the DCDO adlayer to temperatures of 250 K or higher, however, a drastic drop in the CH_2CD_2 desorption yield is observed, even if there is still considerable CH_2CH_2 and CD_2CD_2 desorption. In fact, the yields for both CH_2CH_2 and CD_2CD_2 are approximately constant in the 250–400 K DCDO annealing temperature range, whereas almost no CH_2CD_2 is detected. Only above 500 K the CD_2CD_2 production decreases, because at those temperatures such product is made during the annealing step and before the adsorption of HCHO.

Further evidence for the formation of the dimeric intermediate was obtained from XPS data. Figure 5 shows the C 1s XPS spectra acquired for 2.0 L of adsorbed HCHO as a function of

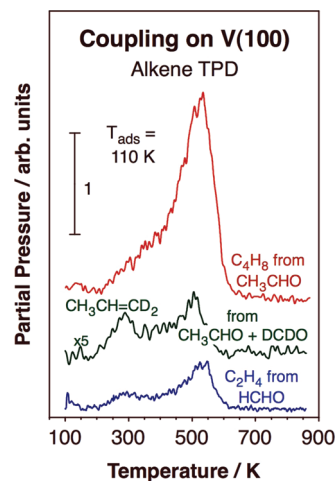


Figure 6. $\text{CH}_3\text{CH}=\text{CHCH}_3$ (top trace), $\text{CH}_3\text{CH}=\text{CD}_2$ (middle trace), and $\text{CH}_2=\text{CH}_2$ (bottom trace) TPD traces obtained from CH_3CHO , $\text{CH}_3\text{CHO} + \text{DCDO}$, and HCHO adsorbed on V(100), respectively, indicating that the coupling of aldehydes to olefins reported here is general and occurs even with different aldehydes (cross-coupling).

annealing temperature. The C 1s XPS signal is initially seen in a peak centered at 286.8 eV, but a red-shift to 285.2 eV is observed upon annealing of that surface to temperatures between 250 and 300 K. That shift is also accompanied by an absolute decrease in signal intensity, signifying the desorption of some carbon-containing species. The loss of surface carbon is clearly associated with the first stage of ethylene production, and the onset temperature for the changes seen in the XPS data coincides with that at which the yield of the mixed-isotope CH_2CD_2 decreases in the experiments summarized in Figure 4. Further heating above 500 K leads to the total removal of the remaining C 1s XPS peak intensity, as also indicated by the detection of a second stage of ethylene production.

The data from Figures 3, 4, and 5 clearly highlight the existence of a surface intermediate between approximately 250 and 400 K responsible for the production of ethylene at 500 K. We suggest that intermediate to be a diolate species, $-\text{OCH}_2\text{CH}_2\text{O}-$. For example, TPD experiments with ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, a reactant that is expected to easily form such a diolate on the surface,⁴¹ indicate the production of ethylene at ~ 505 K (Figure 2b, top trace). Furthermore, the C 1s XPS peak for the diolate produced by thermal activation of ethylene glycol (Figure 5, bottom trace) is centered at the same energy as that observed between 300 and 500 K in the experiments with formaldehyde, 285.2 eV. In general, both TPD and XPS results show similar high-temperature chemistry for formaldehyde and ethylene glycol on V(100), strongly suggesting that both lead to the formation of the same surface intermediate.

The high-temperature alkene formation mechanism identified here seems to be fairly general on V(100). Figure 6 contrasts the ethylene TPD data seen with formaldehyde to similar TPD from two additional cases where the same type of coupling is observed. The top trace corresponds to the formation of 2-butene from thermal activation of acetaldehyde, which peaks at 530 K. Cross-labeling TPD experiments with $\text{CH}_3\text{CHO} + \text{CD}_3\text{CDO}$ similar to those shown in Figure 4 yielded analogous results, with the production of $\text{CH}_3\text{CH}=\text{CDCD}_3$ being completely

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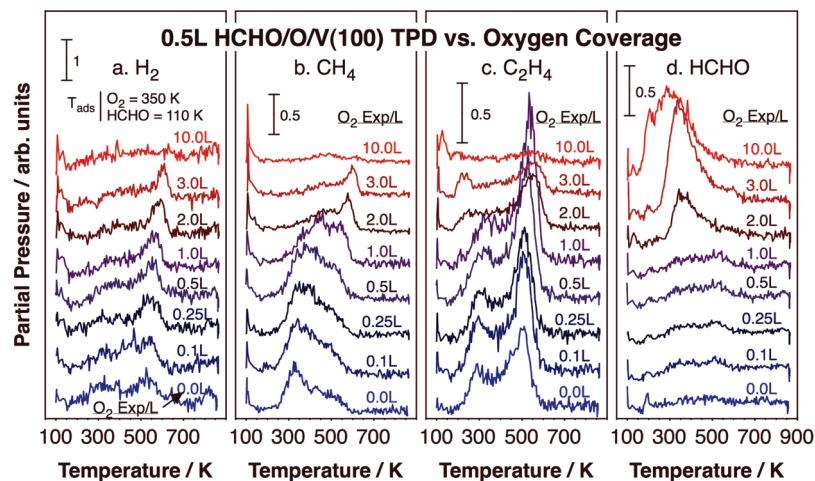


Figure 7. Hydrogen (a), methane (b), ethylene (c), and molecular formaldehyde (d) TPD traces for formaldehyde adsorbed on V(100) surfaces predosed with different amounts of oxygen at 350 K. The main effect of the coadsorbed oxygen is to inhibit all reactions, as manifested by both increases in peak temperatures and decreases in desorption yields.

suppressed if the adsorbed CD₃CDO is activated to temperatures of 300 K or higher before adding the CH₃CHO (data not shown). Cross coupling is also possible,⁴² as indicated by the desorption of CH₃CH=CD₂ from thermal activation of mixed CH₃CHO + DCDO layers (Figure 6, middle trace, $T_{\max} \approx 505$ K). In all these cases, the coupling responsible for the formation of the high-temperature (>500 K) alkene precedes all C–O bond-breaking steps and results in the formation of a surface diolate intermediate.

As reported above, the thermal activation of formaldehyde on V(100) surfaces leads to the production of a number of carbon-containing products, in particular methane and ethylene. On the other hand, no oxygen-containing products other than molecular formaldehyde and carbon monoxide were seen in any of the TPD experiments. This means that oxygen is deposited on the surface by this chemistry, a fact that was indeed corroborated by XPS (data not shown). Given that oxygen insertion steps have been seen on other metals,^{15,16,43–46} that possibility was tested here by performing TPD experiments with formaldehyde dosed on surfaces predosed with varying amounts of oxygen. The O₂ was predosed at 350 K to ensure dissociative adsorption and atomic oxygen formation.^{28,29} For reference, monolayer formation requires approximately 1 L O₂ exposures, and a thin oxide layer forms on the surface after doses above ~ 2 L.²⁹ Figure 7 shows the TPD results obtained for hydrogen, methane, ethylene, and molecular formaldehyde desorption. The main observation here is that adsorbed oxygen inhibits the decomposition of formaldehyde, as indicated by: (1) a decrease in yield for all products, (2) an increase in the reaction temperature for all peaks, and (3) an increase in molecular desorption. It is interesting to note that intermediate coverages of oxygen lead to the almost complete suppression of the low-temperature methylene-coupling step but favor the high-temperature diolate mechanism to ethylene. That is accompanied by a new mechanism for methane (and hydrogen) formation, probably involving the same diolate surface

C₂H₄ formation from HCHO/V(100)

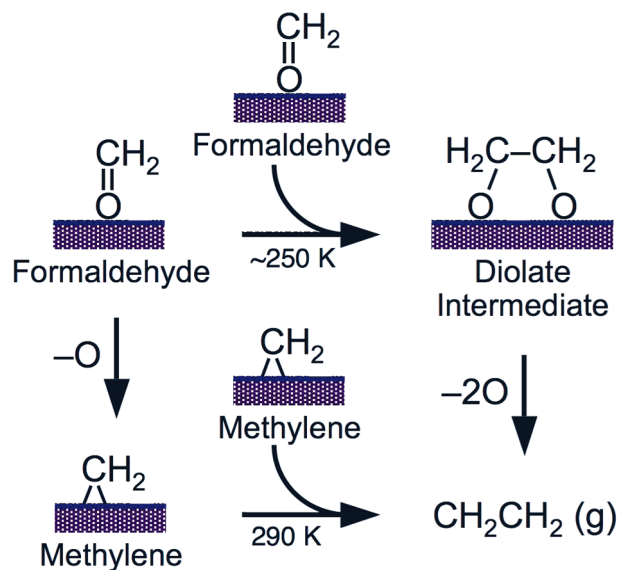


Figure 8. Proposed reaction scheme for the production of ethylene from formaldehyde adsorbed on V(100). Two distinct mechanisms, direct methylene coupling and diolate formation, are indicated for the desorption of ethylene at 290 and 540 K, respectively.

species. No new oxygenated products were detected under any circumstances.

4. Discussion

In this work, the thermal chemistry of formaldehyde on V(100) single-crystal surfaces and under ultrahigh vacuum (UHV) has been characterized in some detail. In general, most of the chemistry observed takes place in two temperature regimes, around 300 and 550 K. Some of the main products detected match those typically seen in thermal decomposition studies on other surfaces. In particular, complete dehydrogenation to hydrogen and carbon monoxide is quite common, and has been reported on Pt(111),¹² Pt(110),⁸ Pd(111),¹⁰ Rh(111),¹⁷ and Cu(100),¹¹ among others. Methane production is also expected, even if that requires hydrogenation of either the

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adsorbed formaldehyde (to methoxide intermediates) or the methylene surface moieties produced by an early C–O dissociation step.

More interesting, because it is less common, is the formation of ethylene. As indicated in the Introduction, such reaction has only been previously reported on TiO_2 ,⁶ $\text{UO}_2(111)$,²³ and $\text{Mo}(110)$ ⁹ surfaces. Ethylene formation in all previous surface-science examples has been explained by a McMurry-type coupling mechanism,³ even if the evidence for that has been limited. The more extensive discussion on this subject has been published by Barteau and co-workers,^{42,47,48} who do not provide direct evidence for C–C coupling preceding C–O bond-scission steps but do make the point that, on TiO_2 at least, the reaction does not occur on metallic Ti^0 centers but rather on low-oxidation titanium ion sites.^{48,49} This is an important point, because it contradicts the initial proposal of McMurry that explains the reactions involving individual inorganic compounds containing zero-valent metals.³ On the other hand, it is consistent with the proposal of V^{2+} as the oxidation state in the vanadium complexes that can promote the reaction.^{1,4} The only example of coupling chemistry on a metal surface is that reported by Friend and co-workers, who also advanced the notion that the reaction involves a diolate intermediate.⁹

Here we report on the formation of ethylene from formaldehyde on a vanadium metallic surface (the metallic nature of the surface was corroborated by XPS experiments, data not shown). Moreover, we provide evidence for two reaction regimes with two different mechanisms of reaction. A diolate intermediate does appear to be key in the formation of ethylene at high temperatures, around 540 K. The key pieces of evidence for that are: (1) the lack of isotope scrambling between HCHO and DCDO in the ethylene produced in TPD experiments where the first of the two reactants is activated on the surface to temperatures above ~ 250 K (Figures 3 and 4); (2) the similarity of the desorption profiles in TPD experiments with formaldehyde and ethylene glycol (Figure 2); and (3) the shift in C 1s XPS peak position upon annealing formaldehyde adsorbed on V(100) to 300 K, to a binding energy similar to that obtained with ethylene glycol annealed to the same temperature.

A second ethylene formation mechanism was also identified at lower temperatures, around 290 K. In that case isotope scrambling was seen, and coupling with methylene groups, produced via activation of adsorbed diiodomethane, is also possible. The most likely scenario here is that of an early C–O bond-breaking step to yield surface methylene moieties followed by coupling of those species on the vanadium surface. It should be noted that: (1) a very similar ethylene desorption profile was observed with diiodomethane adsorbed on V(100) alone (Figure 2);⁴⁰ and (2) the TPD recorded for formaldehyde on V(100) also shows a significant amount of methane production, presum-

ably via hydrogenation of surface methylene or methyl species. Similar methane desorption profiles are seen with methanol.³⁰

Regarding the oxidation state required at the metal center to promote the formation of diolate intermediates, it should be noted that in our experiments the surface always remained in its metallic state, as indicated by XPS. On the other hand, the diolate formation step appears to occur concurrently with the initial decomposition of some formaldehyde into methylene and atomic oxygen on the surface. Moreover, oxygen preadsorption on V(100) significantly shifts the selectivity of ethylene production from the low- to the high-temperature TPD state, that is, from straight coupling of methylene moieties after C–O bond scission to diolate formation. It appears that some coadsorbed oxygen is required to partially modify the electronic nature of the neighboring vanadium surface atoms and promote the dimerization pathway. Moreover, the relative yields for low- versus high-temperature ethylene formation remains approximately constant as the initial coverage of the formaldehyde on the surface is increased. This suggests a complex kinetic behavior for its conversion involving a particular local ensemble of adsorbates. One possibility is a mechanism involving several formaldehyde molecules, where the partition between surface methylene formation and coupling of two formaldehydes to form a diolate may occur in one overall common step (or a sequence of rapid reactions following a rate-limiting step). However, a more detailed study to include the kinetic of formation of other products is needed to settle this issue.

At least two observations reported here are unique to this carbon–carbon-coupling chemistry to produce olefins: (1) two different temperature regimes were identified, with different reaction mechanisms; and (2) the chemistry occurs on vanadium metal centers, although the addition of oxygen may modify the surface to selectively favor the formation of diolate intermediates.

5. Conclusions

The surface chemistry of formaldehyde on V(100) single-crystal surfaces was studied by TPD and XPS. Complete dehydrogenation to hydrogen and carbon monoxide was observed, mainly around 550 K, as on many other metal surfaces. Methane production was also detected, at 355 and 540 K, presumably from hydrogenation of methylene surface species but also possibly via the prior formation of methoxide intermediates. Central to this report is the observation of ethylene desorption in two distinct temperature regimes, at 290 and 540 K. Those follow different reaction mechanisms, as summarized in the scheme in Figure 8: a low-temperature pathway, which most likely involves the direct coupling of surface methylene groups, and a high-temperature reaction, almost certainly requiring the formation of a diolate intermediate.

Acknowledgment. Funding for this project was provided by the U.S. National Science Foundation.

JA9023379

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