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Reactivity and reaction intermediates for acetic acid adsorbed on $CeO_2(1\,1\,1)$

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1. Introduction

Cerium oxide has been widely recognized as a catalytic material and employed in catalytic systems primarily because of its reducibility. This property makes it able to store and release oxygen, and so is used during changes in catalytic cycles in an automotive three-way catalysts. Working with a precious metal catalyst, CeO₂ and especially mixed Ce-based oxides, can buffer oxygen availability during oxidation of CO, reduction of NO, and water gas shift reactions [1]. However, ceria is also interesting for its acid-base properties that make it able to catalyze reactions such as dehydrogenation, ketonization, and dehydration reactions even without the necessity for a catalytic metal [2]. In these reactions that typically involve organic oxygenates, the redox capability of the CeO₂ may enter into the reaction pathways, and this can be expected to lead to a selectivity that varies depending upon the reduction of the ceria surface. It is difficult to discern these changes for polycrystalline CeO₂ under reactor conditions but studies of model surfaces can help relate the reaction selectivity to surface structure, redox

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ABSTRACT

Adsorption and reaction of acetic acid on a $CeO_2(111)$ surface was studied by a combination of ultra-high vacuum based methods including temperature desorption spectroscopy (TPD), soft X-ray photoelectron spectroscopy (sXPS), near edge X-ray absorption spectroscopy (NEXAFS) and reflection absorption IR spectroscopy (RAIRS), together with density functional theory (DFT) calculations. TPD shows that the desorption products are strongly dependent upon the initial oxidation state of the CeO₂ surface, including selectivity between acetone and acetaldehyde products. The combination of sXPS and NEXAFS demonstrate that acetate forms upon adsorption at low temperature and is stable to above 500 K, above which point ketene, acetone and acetic acid desorb. DFT and RAIRS show that below 500 K, bridge bonded acetate coexists with a moiety formed by adsorption of an acetate at an oxygen vacancy, formed by water desorption.

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processes occurring on the surface, and identity of adsorbed surface species present on the surface during reactions.

With this goal in mind, we and others have explored reaction pathways for C1 and C2 oxygenates reacting at single crystal surfaces [3] and CeO₂ nanoparticles with well-defined crystallographic terminations [4,5]. In studies of ethanol dehydrogenation by these CeO₂ nanoparticles, dehydrogenation to acetaldehyde was favored over dehydration to ethylene but the selectivity was found to depend upon surface structure [4]. Sensitivity to structure and to the extent of reduction was found in TPD studies from $CeO_2(100)$ and $CeO_2(111)$ of ethanol and other alcohols [6]. Reactions of acetaldehyde demonstrated weak interactions with a fully oxidized $CeO_2(111)$ but introduction of vacancies by reduction leads to formation of the enolate form [7]. This enolate is identified as an intermediate for coupling reaction to crotonaldehyde, the primary reaction product observed over CeO₂ nanoparticles. During in situ DRIFTS studies of CeO₂ nanoparticles during reaction, targeted to identify reaction intermediates and pathways, it was found that the oxidized product of these reactions, acetate, was frequently observed. This is of practical importance, since it has been shown that carboxylates are the primary intermediate from reactions of aldehydes that lead to long chain ketones via ketonization [8]. Cerium oxide has been shown to ketonize acetic acid to acetone, but depending upon conditions the ceria can undergo transformation to form bulk cerium acetate [9]. Mechanisms for ketonization of carboxylic acids and the acid enolization pathway

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leading to ketone have been of intense interest and are still a matter of debate [10–12]. Clarification of acetate and its role as spectator, intermediate or deactivator can be aided by model studies aimed at identifying the temperature evolution of adsorbed acetic acid. Identification of surface intermediates by IR methods during C2 reactions requires better identification of possible reaction intermediates by their spectroscopic signature. First principles density functional theory (DFT) calculations now make it possible to examine bonding configurations of surface intermediates in detail when combined with surface science techniques. Comparisons of vibrational spectra simulated using DFT calculations with experimental FTIR spectra obtained for formate, carbonates and acetaldehyde have clarified the interpretation of the experimental spectra, which enables more reliable detection of the surface species [7,13,14].

To obtain a better understanding of the interactions between acetic acid and cerium oxide catalysts, we have now combined UHV based measurements on a model $CeO_2(111)$ surface with DFT computations. Surface science measurements, performed as a function of temperature on a surface with known structure, provide information about the evolution of the acetic acid on the surface and provide signatures of bonding configurations. DFT is used to predict models for the surface bonding configurations and to simulate vibrational spectra that can be compared directly with experimental RAIRS spectra. From this we have identified the stages of acetic acid deprotonation and decomposition. Measurements are performed upon both oxidized and reduced surfaces to identify the important role of oxygen vacancies upon the reaction products. From these studies, we find that bridge bonded acetate coexists with another type of acetate that is bonded by its interaction with oxygen vacancies.

2. Experimental and computational methods

Experiments were performed in three separate ultra-high vacuum chambers described previously, one used for reflection absorption infra-red spectroscopy (RAIRS) [7], one based at the National Synchrotron Light Source (NSLS) for soft X-ray photoelectron spectroscopy (sXPS) and near edge X-ray absorption fine structure (NEXAFS), and a third for performing temperature programmed desorption (TPD). In each of the UHV systems the model CeO_2 catalyst were prepared as thin films deposited on Ru(0001)single crystals, leading to a flat CeO₂ surface with (111) orientation [15]. Briefly, cerium metal is evaporated from a metal doser onto the Ru crystal held at 700 K while under a controlled pressure of oxygen gas, typically around 10^{-7} torr. By varying the oxygen pressure, a range of catalyst with different ratios of Ce³⁺/Ce⁴⁺ could be obtained, as quantified from the XPS spectra (Supplemental information, Fig. S1). Reduced surfaces could also be obtained by exposure to methanol at ~700 K [16]. Glacial acetic acid was degassed by several freeze-pump-thaw cycles and dosed onto the surface through either a directed, effusive gas doser or a leak valve.

Temperature programmed desorption (TPD) experiments were performed using a temperature ramp rate of 2 K/s while biasing the sample at -70 V to prevent electrons generated by the mass spectrometer ionizer from stimulating reactions at the surface. For the TPD spectra, the prepared surfaces were exposed to acetic acid from a directed doser at 175–185 K, chosen to be slightly higher than the multilayer desorption temperature. Following dosing, the sample is positioned in front of the quadrupole mass spectrometer (Hiden HAL/3F 301) and the QMS signal at multiple masses was monitored during the temperature ramp. The intensities of the observed products were scaled according to the method described by Ko et al. [17]. The masses used and the product that they most represent are H₂ (m/z = 2), water (m/z = 18), acetylene (m/z = 26), acetaldehyde (m/z = 29), ketene (m/z = 42), acetone (m/z = 43 and 58), acetic acid (m/z = 45 and 43), CO (m/z = 28) and CO₂ (m/z = 44). In the TPD spectra shown and in their peak integration, interferences from overlapping co-products were subtracted. Various other possible products were monitored but were not definitively detected, including methane, formaldehyde, dimethyl ether and diethyl ether, vinyl acetate, methyl acetate, ethyl acetate, and various alcohols.

RAIRS was performed as described previously [7]. Spectra were collected using grazing angle ($\sim 86^{\circ}$) p-polarized light from the IR beam of a Mattson Infinity infrared spectrometer, and the reflected IR beam was detected with a liquid-nitrogen cooled MCT detector. All spectra shown are differences between the IR absorption spectrum at a certain condition and a reference spectrum recorded for the clean ceria surface. All spectra were collected at an instrumental resolution of 4 cm^{-1} and the signal averaged for 1024 scans.

Soft X-ray photoelectron spectroscopy (sXPS) was conducted using synchrotron radiation on beamline U12a at the National Synchrotron Light Source (NSLS). The XPS data were collected using a VSW 125 hemispherical analyzer with the sample oriented such that the photon incident angle was 35° and electron emission angle was 30° relative to the surface normal. C 1s and O 1s spectra were recorded using photon energies of 400 and 600 eV, respectively. The instrumental resolution was ca. 0.5 eV. The Ce 4d photoemission was used for binding energy calibration using the 122.3 eV satellite feature. The Ce oxidation state was determined using XPS of the Ce 4d regions at Beamline U12a.

NEXAFS was performed at the C k-edge. The energy resolution was less than 0.5 eV and the photon energy was calibrated using the dip in the photon flux at 284.7 eV [18]. The X-ray absorption was recorded using a partial yield electron detector. The high-pass retarding grid was set at -230 V. Higher order X-ray excitation created apparent absorption features from the ceria substrate due to the 0 k-edge and the Ce M_{IV} and M_V edges. The absorption due to only higher order radiation was determined by recording spectra with a retarding grid voltage of -307 V, i.e. greater than the first-order photon energy. The background resulting from the higher order excitation was subtracted from the NEXAFS spectra.

Periodic, spin-polarized DFT calculations were performed within the generalized gradient approximation (GGA-PW91) [19] using the Vienna Ab initio Simulation Package (VASP) [20–22]. DFT at the GGA level fails to properly describe the localization of the Ce 4f electrons that occurs with the reduction of Ce^{4+} to Ce^{3+} due to self-interaction errors [23]. To compensate for this deficiency, the DFT+U formalism of Dudarev et al. [24] was used. It is an efficient, ad hoc method that directly modifies the on-site Coulomb interaction, which has been shown to satisfactorily reproduce localized f states in bulk Ce_2O_3 and in oxygen vacancies in CeO_2 , although no single value of U can simultaneously improve the predictions for all properties of bulk CeO_2 and Ce_2O_3 [25,26]. A U-value of 2 was used in this study based on our previous results in modeling the adsorption of formate and acetaldehyde on $CeO_2(111)$ [7,14].

The core electrons were described by the projector-augmented wave method (PAW) [27], and the Kohn–Sham valence states (including Ce(4f5d6s), O(2s2p), C(2s2p), H(1s)) were expanded in a plane wave basis up to a kinetic energy of 400 eV. The CeO₂(111) surface was represented by a slab consisting of three O–Ce–O trilayers with a (2×2) surface unit cells, which corresponds to ¼ monolayer (ML) of coverage for each adsorbate per unit cell.

The periodic slabs were separated in the *z* direction by ca. 12 Å of vacuum. The top trilayer and all adsorbates were fully relaxed and the remaining two trilayers were held fixed at the bulk positions. Adsorption was allowed on one side of the slab only, with dipole decoupling [28] in the *z* direction. The surface Brillouin zone was sampled with a $2 \times 2 \times 1$ Monkhorst–Pack kpoint grid [29]. Geometry optimization was converged to below 0.01 eV/Å in each degree of freedom for all relaxed atoms. Different

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Fig. 1. TPD spectra obtained following exposure to acetic acid at 175 K on fully oxidized CeO₂. Spectra are offset for clarity.

spin states were calculated and the lowest adsorption energy was reported for each adsorbate. The adsorption energy was calculated as $\Delta E = E_{\text{total}} - E_{\text{slab}} - E_{\text{mol}}$, where E_{total} , E_{slab} , and E_{mol} are the energies of the surface with an adsorbate, the clean surface without adsorbate, and the adsorbate molecule isolated in the gas phase in a neutral state (closed-shell or radical).

The vibrational frequencies and simulated IR spectra of surface adsorbates were calculated using the Atomic Simulation Environment [30]. The vibrational modes and frequencies were calculated from a finite difference approximation of the dynamical matrix, and the IR intensities were calculated from a finite difference approximation of the gradient of the dipole moment in the *z* direction [31]. The magnitude of the displacement was 0.01 Å in each degree of freedom. The assignments of the calculated modes were based on visual inspection. Additional details of the setup of our DFT calculations can be found in Refs. [7,14].

3. Results

3.1. Desorption products

TPD experiments were performed on ceria samples with different levels of reduction. Fig. 1 shows the TPD obtained from the fully oxidized surface following adsorption at 175 K. Acetic acid (mass 45) desorbs in two states near 210 K and 520 K. Acetic acid fragmentation pattern presents two intense fragments at 43 and 45 amu and a less intense parent peak at 60 amu. All three masses were followed to discriminate against acetone which would contribute at mass 43. The lower temperature state corresponds to desorption of undissociated, chemisorbed acetic acid molecules and the high temperature peak presumably corresponds to recombination of acetate with its proton bonded on nearby O anions (Ce–OH). Water also desorbs in multiple peaks, including a sharp peak at



Fig. 2. TPD spectrum following exposure to acetic acid at 175 K on a surface that is 60% reduced, i.e. corresponding to a surface stoichiometry of CeO_{1.7}. Spectra are offset for clarity.

310 K. Ketene, the primary C₂ product, desorbs at 590 K along with H₂O. These correlated products imply cleavage of a C–O bond and of a methyl C-H bond, although it cannot be determined from these data which is rate limiting. A trace amount of acetone is detected at nearly the same temperature as the ketene. Formation of acetone implies a coupling reaction such as ketonization between nearby acetates. Acetone is the only coupling product observed. At higher temperatures (above 600 K) CO and CO₂ desorb in broad states implying C-C bond breaking occurs. Small amounts of acetylene were detected at 700 K, but methane is not observed at any point of the TPD experiments. To speciate the O in the water desorption, a fully oxidized film of Ce¹⁸O₂ was grown and used as a substrate for TPD of CH₃C¹⁶O₂H. As shown in Fig. S3 (Supplemental Information) the majority of H₂O desorbing at 210 and 310 K extracts O from the lattice, while the water desorbing near 590 K derives in equal parts from lattice oxygen and from acetic acid.

Several TPD experiments were run on a ceria surface that was reduced, either by sequential dosing and flashing of acetic acid or by treatment with methanol at 700-900 K (for example, Fig. S2, see SI). Acetic acid TPD performed from a surface that is 60% reduced, i.e. corresponding to a surface stoichiometry of $CeO_{1,7}$, is shown in Fig. 2. The product distribution is substantially different than for the fully oxidized surface. Desorption of undissociated acetic acid is still visible below 300 K, but there is no desorption of H₂O at or below 300 K as seen from the oxidized surface. Recombinative desorption of acetic acid, seen at 510K for the oxidized surface, does not occur from this highly reduced surface at any temperature. There is also less ketene and acetone formed compared to the oxidized surface, although there is increased acetaldehyde that desorbs at 550 K just below the H₂ desorption temperature. Desorption of CO and CO₂ at 600–700 K is decreased compared to the oxidized surface and little or no CO₂ is observed up to 900 K.

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Fig. 3. Integrated TPD products are shown as a function of the extent of oxidation of the surface. The intensities shown for acetone, acetaldehyde and acetic acid are scaled by a factor of 5.

Desorption of H_2 increases substantially compared to the oxidized surface, peaking strongly at 600 K. It has been previously reported [32] that hydroxyls (from water) are stabilized on a reduced surfaces of ceria, leading to desorption of H_2 (rather than H_2O) above 500 K as seen prominently in this case. The amount of acetylene detected at ~700 K is increased somewhat compared to the fully oxidized CeO₂. A portion of the remaining C containing species are consumed by reacting with lattice oxygen at high temperatures (above 800 K) liberating mainly CO and not CO₂, probably because of the decrease of available O on the reduced surface.

The variation in product distribution as a function of the extent of reduction of the initial CeO_2 surface is shown in Fig. 3. The oxidation state of the Ce is determined from the Ce 3d XPS (see Supplemental Information). To avoid inclusion of physisorbed acetic acid, the acetic acid product is integrated over only the high temperature desorption peak.

3.2. Adsorption states

3.2.1. sXPS

sXPS spectra were recorded after the fully oxidized $CeO_2(111)$ was exposed to $10L(1L = 10^{-6} \text{ torr s})$ of acetic acid at 100 K and then annealed to sequentially higher temperatures, shown in Fig. 4. At the lowest annealing temperatures, the C 1s spectrum (Fig. 4 lower panel) shows two peaks near 290.2 and 286.1 eV. A shoulder is evident at 289 eV and upon annealing to 200 K this shoulder becomes the dominant feature with a loss of the peak at 290.2 eV. It may be assumed that the transition upon annealing to 200 K is associated with loss of multi-layer, physisorbed acetic acid, and possible deprotonation of the remaining chemisorbed acetic acid. Most of the physisorbed acetic acid desorbs leaving primarily two features peaked at 289.1 and 285.7 eV that are assigned to the carboxyl and the methyl carbons. However, peak fitting suggests that shoulders are evident on the high binding energy side of both peaks. As the sample is annealed to 400 K, both features appear to sharpen and shift to higher binding energy. The intensity of both peaks decreases

as the sample is annealed to 500 K and above, but a small new feature appears at 285 eV that can be assigned to a reduced form of carbon. By 600 K the carboxylate and methyl peaks are essentially gone and only small amounts of the reduced carbon remain. All of the C is gone after annealing to 900 K.

From the peak fitting of the two components in the methyl (at 286.4 and 285.8 eV) and carboxylate (at 290.0 and 289.1 eV), the amounts of each type of carbon can speciated and are summarized in Fig. 5 as a function of the annealing temperature. The transfer of intensity from the lower binding energy components to the higher energy components occurs over the temperature range 200–400 K, the range where water desorbs from the surface (Fig. 1). Desorption of water creates O-vacancies on the surface possibly allowing the acetate to shift to a different adsorption site or to change configuration.

The corresponding O 1s spectra are shown in Fig. 4 (upper panel). The peak at 530.4 eV, due to ceria lattice O, is attenuated by the adsorbate at 200 K, and an adsorbate related peak appears at 532.2 eV with a tail on the higher binding energy side. Upon annealing to 300 K the tail disappears while there is a 0.4 eV shift in the adsorbate peak to 532.6 eV. This peak further shifts and sharpens at 400 K. The loss of intensity on the low binding energy side likely reflects the loss of surface OH through water desorption that occurs in this temperature range (see Fig. 1) while the loss of the high binding energy tail is due to desorption of the molecular (undissociated) acetic acid. The temperature-dependent loss of all adsorbate oxygen (OH and other O-containing molecules) is shown in Fig. 5. As the sample is annealed above 500 K the intensity drops dramatically as O-containing products desorb from the surface or the O incorporates into lattice. The O 1s intensity approximately tracks the total C 1s intensity above 300 K. However, at 600 K the adsorbate O 1s peak is gone whereas there is still some residual, reduced carbon present.

Fig. 6 shows sXPS spectra following adsorption of acetic acid on partially reduced $CeO_2(111)$. In this case the sample was approximately 60% reduced ($CeO_{1,7}$) and was exposed to a 10L dose

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Fig. 4. sXPS of the O 1s region (A) and the C 1s region (B) obtained following adsorption of acetic acid on oxidized ceria at 200 K and subsequent annealing to sequentially higher temperatures.

of acetic acid at 100 K and subsequently heated to sequentially higher temperatures. Upon heating to 200 K there are two prominent peaks in the C 1s spectra (Fig. 6 lower panel) at 287.4 eV and 291.0 eV, with shoulders clearly evident on the high binding energy side of both peaks. As on the fully oxidized surface the low and high binding energy peaks are assigned to the methyl and carboxyl,



Fig. 5. Speciation of surface carbon and total adsorbate O by sXPS following heating adsorbed acetic acid adsorbed on a fully oxidized $CeO_2(111)$ surface. Values obtained from integration of C 1s and O 1s features in Fig. 4.

respectively, in acetate. As the sample is annealed the nominal peak positions shift to higher binding energy and the peaks become narrower and more symmetric. At 500 K new features are evident on both higher and lower side of the methyl peak. Upon annealing the sample to 550 K the intensity of the carboxylate feature decreases dramatically, the peak positions of the methyl and carboxylate shift to lower binding energy, and the new features at 288.6 eV and 286.3 eV grow. The peak near 288.6 is poorly resolved and may consist of a dioxy species or an enolate. The peak at 286.3 eV is assigned to a CH_X species possibly bound to Ce [33,34]. As the sample is annealed to 900 K all of the C 1s peaks disappear except an intense peak at 286 eV. This peak could only be removed by oxygen treatment at elevated temperature.

In the O 1s spectra (Fig. 6 upper panel), adsorption and annealing to 200 K leads to a broad adsorbate peak centered at 533.3 eV. As on the oxidized surface, there are shifts and sharpening of the adsorbate peak as the sample is annealed to higher temperatures, but the overall O 1s intensity (acetate and hydroxyl) remains constant from 200 K to 500 K. After annealing to 550 K the adsorbate intensity drops and the peak shifts to 533 eV. These changes in the adsorbate O 1s feature correspond to loss of the carboxylate and growth of the alkoxy in the C 1s spectrum (Fig. 6A). Only the lattice O feature remains at 900 K indicating that the C that remains on the surface is not bonded to O.

3.2.2. RAIRS

RAIRS was performed to get additional information about the nature of the bonding and the bonding configurations of the acetates. In Fig. 7 (lower panel), the RAIRS spectra in the region of the C=O and OCO stretches are shown following a sequence of exposures at 175 K. The surface was held at constant temperature, so the coverage increases to saturation (Fig. 7) at the highest dose. Prior to exposure, the surface was fully oxidized by heating to 700 K in 10^{-7} torr O₂. A feature at 1430 cm^{-1} is most prominent at low coverage, but features at 1530 and 1695 cm⁻¹ become more obvious with increasing coverage and a feature at 1450 cm⁻¹ dominates at the highest coverage. Following the exposure the saturated surface was subsequently annealed to sequentially higher temperatures following the adsorption as shown in Fig. 7 (upper panel). After annealing to 226 K, the spectrum is dominated by a strong feature peaking at 1450 cm⁻¹, although it appears to have shoulders and it is accompanied by a peak at $1695 \,\mathrm{cm}^{-1}$. Upon annealing to 326 K the peak at 1695 cm^{-1} disappears, the strong

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Fig. 6. sXPS of the O 1s region (A) and the C 1s region (B) obtained following adsorption of acetic acid on reduced ceria at 200 K and subsequent annealing to sequentially higher temperatures.

peak at 1450 cm^{-1} decreases and its shoulders resolve into two peaks at higher and lower wavenumbers. In addition, two sharp features at 1330 and 1390 cm⁻¹ appear. Further annealing to 527 K removes all traces of the 1450 cm⁻¹ peak, and four prominent peaks remain in the RAIRS spectrum. A further anneal to 627 K removes all traces of these peaks (not shown).



Fig. 7. Lower: evolution of RAIRS spectra with coverage obtained by exposing a fully oxidized $CeO_2(111)$ surface to acetic acid at 175 K with sequential doses to saturation. Upper: evolution of RAIRS spectra from the saturated surface during subsequent annealing to temperatures indicated in the plot. Spectra are difference spectra (relative to clean surface), background subtracted and offset vertically.

The nature of the four features remaining at 527 K can be further elucidated by observing acetic acid on the reduced surface as shown in Fig. 8. This surface was 60% reduced (to CeO_{1.7}). Sequential exposures to acetic acid at 175 K were used to increase the coverage while monitoring RAIRS. At the initial adsorption two peaks are obvious at 1330 and 1396 cm⁻¹, while a weaker shoulder is apparent at about 1430 cm⁻¹ (Fig. 8 lower panel). These three features align nearly perfectly with features observed after annealing the acetic acid adsorbed on the fully oxidized surface to 527 K (Fig. 7). As exposure increases, these peaks grow in intensity but remain at roughly the same position (or red shift less than 3 cm^{-1}). At the highest coverage the peak at 1423 cm⁻¹ grows to dominate the spectrum, and it is accompanied by a peak at $1705 \,\mathrm{cm}^{-1}$. Growth of these two peaks at highest coverage is approximately correlated, and may be associated with an additional adsorbate state that differs from that observed at the lowest coverage.

3.2.3. NEXAFS

C k-edge NEXAFS spectra were recorded after oxidized $CeO_2(111)$ and reduced $CeO_{1.7}(111)$ were exposed to 10 L of acetic acid at 90 K and then annealed to higher temperature. The spectra from fully oxidized $CeO_2(111)$ are shown in Fig. 9A and the spectra from reduced $CeO_{1.7}(111)$ are shown in Fig. 9B. The upper spectrum in Fig. 9A was recorded immediately after adsorption at 90 K

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Fig. 8. Lower: evolution of RAIRS spectra with coverage obtained by exposing a partially reduced $CeO_{1,7}(111)$ surface to acetic acid at 175 K with sequential doses to saturation. Upper: evolution of RAIRS spectra from the saturated surface during subsequent annealing to temperatures indicated in the plot. Spectra are difference spectra (relative to clean surface), background subtracted and offset vertically.

and is from a multilayer of acetic acid. A number of adsorption resonances are evident and have been labeled in accordance with the absorption spectrum reported for gas phase acetic acid by Robin et al. [35]. When the sample was annealed to 300 K the multilayer acetic acid desorbs and many of the minor features are no longer evident but the π^* resonance from the carboxylate is still dominant at 288.2 eV. The peak position has shifted to a slightly lower photon energy compared to the multilayer, consistent with the lower C 1s sXPS binding energy of acetate relative to acetic acid.

After annealing at 550 K the π^* resonance from the carboxylate is weaker due to the loss of carboxylate as observed in the C 1s sXPS spectra (Fig. 4). This temperature corresponds to the high temperature desorption of acetic acid and the onset of ketene desorption (Fig. 1). A new feature emerges in the NEXAFS near 286.5 eV, labeled (*) in Fig. 9A. Peaks near this position are generally associated with a π^* resonance from a carbonyl [18]. However, carbonyl is not indicated at 550 K in the C 1s sXPS spectrum (Fig. 4). Previous studies with acetaldehyde, formaldehyde and acetone on oxidized CeO₂(111) placed the carbonyl binding energy between 288.0 eV and 288.5 eV [33,36,37]. Alternatively, the NEXAFS peak may be associated with a π^* C=C resonance such as found in enolate or a ketene-like intermediate that is more clearly evident on the reduced surface (see below).

When the acetic acid is adsorbed on reduced CeO_{1.7}(111) and annealed to 300 K the NEXAFS spectrum (Fig. 9B) is dominated by the π^* CO resonance associated with carboxylate, as for the case of



Fig. 9. NEXAFS at the C 1s edge, A) on fully oxidized, and B) on highly reduced ceria. In B, the $\pi^*(C=C)$ resonance at 284.6 eV is associated with a C at the alkyl end ($-C=\underline{C}H_2$) and the $\pi^*(C=C)$ resonance at 286.4 eV is assigned to the oxygenated C ($-OO\underline{C}=CH_2$ or $O\underline{C}=CH_2$).

the fully oxidized surface (Fig. 9A). After annealing to 550 K this resonance decreases and new peaks appear at 286.4 eV and 284.6 eV, but the total C absorption intensity, indicated by the magnitude of the "jump" between 283 eV and 305 eV, is roughly unchanged. The NEXAFS indicates that the acetate has converted to a new species. Two likely candidates are (CH₂=COO_{ad}) and (CH₂=CHO_{ad}). The former, (CH₂=COO_{ad}), has been described previously as a "surface ketene" formed from enolization of acetate [38], a surface acetic acid dianion intermediate [11], or a dioxyketene [39]. The latter, (CH2=CHOad), corresponds to enolate as has been previously observed from adsorption of acetaldehyde [7,40] and ethylene glycol [41] on reduced $CeO_x(111)$. The two new peaks in the NEXAFS are assigned to π^* (C=C) resonances, in either the surface ketene or the enolate, with the peak at 284.6 eV associated with a C at the alkyl end $(-C=CH_2)$ and the peak at 286.4 eV assigned to the oxygenated C (-OOC=CH₂ or OCH=CH₂) [42]. Similar NEXAFS spectra have been observed from enolate formed by acetaldehyde adsorption on CeO₂(111) [40], and on CeO₂(100) [39]. On the CeO₂(100) both enolate and dioxyketene (surface ketene) formation was proposed based upon the sXPS.

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Fig. 10. DFT-calculated minimum-energy structures for various states of acetate on $CeO_2(111):(A)\mu$ -acetate; (B) μ -acetate co-adsorbed with H; (C) acetate/V₀; (D) acetate/V₀ co-adsorbed with H; (G) CH_2 =COO/V₀; (H) CH_2 =COO/V₀). In each panel, side view is on left and top view is on right. Large brown; medium green, red, and black; and small white spheres represent lattice O, lattice Ce, O, C, and H atoms, respectively. Top-layer lattice O atoms are colored more lightly to be distinguished from lower-layer lattice O atoms. Medium orange spheres in panels (B), (D), and (F) represent coadsorbed H atoms that form surface hydroxyl groups. Bonds between O in acetates and lattice Ce are for illustrative purposes only. Molecular images are made using VESTA [60].

After the sample is annealed to 700 K the absorption peak at 285 eV increases while the other peaks decrease. At this temperature, the C 1s spectrum (Fig. 6A) indicates that there are no C–O bonds remaining. This implies that the NEXAFS peaks have changed and are no longer due to carboxylate or enolate as assigned at 550 K. Instead the peaks at 285 eV, 286.7 eV and 288.2 eV are consistent with a carbonaceous deposit containing unsaturated C–C bonds. Similar spectra have been observed for C60 fullerenes [43] and amorphous C films [44]. The spectrum has some similarities with NEXAFS spectra from metal carbides [45] however metal carbides generally have C 1s XPS binding energies near 282–283 eV [46]. Therefore cerium carbide is ruled out based on the C 1s spectrum in Fig. 6A.

3.2.4. DFT

A number of different acetate states on both the fully oxidized and the partially reduced $CeO_2(111)$ surfaces were examined. The latter was represented by a point oxygen vacancy (denoted V_o) or a dimer of oxygen vacancies (denoted by VV₀) in the surface oxygen layer of the $CeO_2(111)$ slab, as we have done previously [7,14]. Several of these states possess IR-active modes that are consistent with the various observed RAIRS spectra. The energy-minimized structures of these states are shown in Fig. 10, including bridging (μ) acetate (located atop a pair of adjacent Ce⁴⁺ sites; Fig. 10A); μ -acetate co-adsorbed with H (Fig. 10B); acetate adsorbed in an oxygen vacancy (acetate/ V_0 ; Fig. 10C); acetate/ V_0 co-adsorbed with H (H bonded to a lattice O; Fig. 10D); acetate/V_o co-adsorbed with μ -acetate (Fig. 10E); acetate/VV_o co-adsorbed with H (Fig. 10F); CH₂=COO adsorbed in an oxygen vacancy (CH₂=COO/V₀; Fig. 10G) and in a vacancy dimer (CH₂=COO/VV₀; Fig. 10H) respectively. The adsorption energies of these states are reported in Table 1. The simulated IR spectra for these species are shown in Fig. 11A and B.

4. Discussion

The combination of desorption measurements and surface spectroscopies allows us to put together a detailed description of the transformations that acetic acid undergoes on a CeO₂ surface as shown in Scheme 1. This scheme summarizes the desorption products that are observed and shows in an approximate way the adsorbate species and their evolution with temperature. It is clear that lattice oxygen participates in the temperature-dependent transformations and that oxygen vacancies play an important role both in stabilizing and in altering surface adsorbates. Depending on temperature and extent of reduction of the ceria, as it affects oxygen availability, the acetic acid can desorb intact or decompose all the way to H_2 , CO, and carbonaceous surface deposits. More interesting are the pathways and surface intermediates that lead to other C1, C2 and C3 desorption products.

Adsorption at 175 K on a fully oxidized CeO₂ surface leads to accumulation of molecularly adsorbed, undissociated acetic acid. This conclusion is clear from the RAIRS spectrum (Fig. 7) which shows characteristic peaks that can be assigned as v(C=0) at 1695 cm⁻¹, δ (CH₃) at 1430 cm⁻¹, υ (C–O) at 1190 cm⁻¹, and CH₃ rock at 1020 cm⁻¹. These positions approximately match with gas phase (or liquid phase) acetic acid [47–49] although the presence of OH bending mode is not obvious and this mode may be most affected by adsorption and interactions with the surface and neighboring molecules. Annealing the oxidized surface to 226 K removes most indications of the acetic acid, consistent with its desorption seen in TPD at 200 K (Fig. 1). Not all adsorbate is acetic acid at 175 K and the sXPS implies that deprotonated acetate is present as early as 150 K. Coexistence of acetic acid and acetate explains the peaks in the C1s sXPS spectrum and their changes between 150 and 200 K (Fig. 4).

After desorption of weakly bonded molecular acetic acid, it is generally assumed that dissociated acetic acid remains on the surface in the form of acetate [50,51], but the RAIRS data suggest that more than a single state remains. Following anneal to 326 K, the RAIRS features sharpen up and two new modes appear at 1330 and 1390 cm⁻¹, separated by 60 cm^{-1} . These two lower wavenumber modes grow in intensity even as the modes at higher wavenumber (1430 and 1465 cm⁻¹) persist, suggesting that at least two types

Table 1

DFT-calculated adsorption energies (in eV) of the various acetate states included for comparison with experimental IR spectra.

State	$\Delta E (eV)$	
μ-Acetate ^a	-0.77	
μ-Acetate + H ^b	-0.95	
Acetate/V _o ^a	-4.18	
Acetate/V _o + H ^b	-2.50	
Acetate/V ₀ + μ -acetate ^a ,*	-3.28	
Acetate/VV _o + H ^b	-2.71	
CH ₂ =COO/V _o ^c	-1.09	
CH ₂ =COO/VV _o ^c	-1.34	

^a With respect to gas-phase acetate.

^b With respect to gas-phase acetic acid.

^c With respect to gas-phase ketene.

* Averaged over two acetate groups



Fig. 11. Comparison of experimental and computed spectra for structures proposed for acetate on the oxidized (A) and reduced (B) surfaces of CeO₂. Computed spectra are stable structures found by DFT and described in Fig. 10 (see text: "+" indicates co-adsorption of two species). Experimental spectrum in A is for acetic acid adsorbed on fully oxidized CeO₂ followed by annealing to 527 K; experimental spectrum in (B) is for acetic acid adsorbed on CeO_{1.7} followed by annealing to 444 K. Spectra are offset vertically and the experimental spectra are arbitrarily scaled.

of adsorbates are coexisting. Annealing to 326K must also lead to desorption of water, as demonstrated by the TPD that features water desorption at 310 K (Fig. 1). It is apparent that much of this water derives from reaction of the dissociated acid proton with lattice oxygen, a conclusion supported by the desorption experiments performed on the Ce¹⁸O₂ film that indicate that the desorbing water contains lattice oxygen (Fig. S3). Therefore during the TPD, water desorption leads to reductive oxygen vacancy formation on the surface. Reduction of the surface by the loss of water explains the shift in the sXPS positions to higher binding energies when the oxidized surface is annealed from 300 to 400 K [40]. The resulting vacancies become traps for surface acetates, which may migrate a short distance to adsorb there in a more stable configuration. Further evidence for this interpretation derives from the adsorption on the pre-reduced surface, which exhibits the same two modes $(1330 \text{ and } 1390 \text{ cm}^{-1})$ already at the lowest exposures (Fig. 8). We

conclude that these modes are associated with acetate adsorption at a vacancy. However, there is another sharp mode at 1465 cm⁻¹ that remains after annealing to 527 K (Fig. 7). This feature is not observed during the initial stages of adsorption on the reduced surface, and so it must be distinguished from those associated with the adsorbate trapped at the vacancies. Although the sXPS indicates two types of C present at 500 K, consistent with carboxyl and methyl of acetate, sXPS alone cannot differentiate two structurally distinct acetate-like adsorbates. However, the NEXAFS at the C 1s edge indicates a new resonance at 286.5 eV that grows between 300 and 500 K. It is associated with another type of π hybridized bonding that is distinct from the π^* CO of acetate.

The challenge is to identify more definitively the two types of adsorbates, and the modes observed in the RAIRS provide insights. Previous compilations of IR vibrational data for metal carboxylates, including acetate complexes, have described them by characteristic symmetric and asymmetric OCO modes and their splitting $\Delta = v_a - v_s$ [52,53]. Although there are difficulties in postulating structure from the positions of the modes, values of Δ that are significantly less than *ionic values* are indicative of chelating or bridging bidentate bonding [52]. Sodium acetate in solution exhibits values of Δ around $140\,cm^{-1}$ between the υ_a mode at 1560 cm⁻¹ and the v_s manifold that peaks at 1420 cm⁻¹ [54,55]. The splitting between the strongest observed modes is 60 cm⁻¹ on the reduced surface (at 1330 and 1390 $\rm cm^{-1})$ either before annealing at low coverage or after annealing to 444 K (Fig. 8). The two peaks are also dominant features on the oxidized surface (Fig. 7). This splitting is considerably smaller than the ionic values for Δ . Based upon the compilation of Deacon [52], the asymmetric mode, $v_a(OCO)$, is expected to be found at wavenumbers ranging from about 1525 to 1575 cm⁻¹ for chelating acetate and roughly 1530 to 1630 cm⁻¹ for bridging acetates, a range that includes the solution value of 1560 cm⁻¹. Unidentate acetate groups are typically higher still. Similarly, solid Ce acetate itself shows a peak at 1564 cm⁻¹ [9] and acetic acid adsorbed on polycrystalline CeO₂ leads to a peak 1540 assigned to $v_a(OCO)$ consistent with other tabulated acetates [56]. All of these values are higher than the most prominent modes seen on the oxidized surface at $1450-1465 \text{ cm}^{-1}$ (Fig. 7) or on the pre-reduced surface at 1425 cm⁻¹ (Fig. 8), suggesting that these adsorbates are more strongly interacting with the CeO₂ than typical acetate.

Based on the evidence from RAIRS we postulate that there are at least two types of acetate on the oxidized surface in the temperature from around 300K up to the onset of ketene and acetone desorption above 500 K. The apparently low wavenumbers of the O-C-O modes suggest a strongly bonded µ-acetate remaining on oxidized parts of the surface, where it is preferentially located above a pair of Ce⁴⁺ sites (Fig. 10A). H₂O removal below 300 K suggests acetate adsorbed in an oxygen vacancy (acetate/V₀)(Fig. 10C). Another possibility is co-adsorbed µ-acetate and acetate/ V_0 (Fig. 10E) because the surface coverage of acetate is likely to be high before decomposition begins substantially. The simulated IR spectra for these three configurations are presented in Fig. 11A. The computed IR-active modes in the range of 1260–1390 cm⁻¹ correspond to $v_s(OCO)$ and $v_a(OCO)$ with considerable variation in position, while the modes from near 1430 cm⁻¹ correspond to CH₃ scissor. Qualitatively these features are fully consistent with the three broad features observed at 1330, 1390, and $1430 \,\mathrm{cm}^{-1}$ at 527 K (Fig. 7). Note that the computed spectrum for acetate/V₀ exhibits two strong peaks split by 49 cm^{-1} (Fig. 11A) consistent with the observed Δ (60 cm⁻¹) for the vacancy stabilized acetate described above.

On the reduced surface, TPD indicates that there is no exit channel for hydrogen either as H_2 or H_2O below ~ 500 K. Therefore the surface is H- and defect-rich until the onset of H_2 desorption above 500 K. Two acetate states co-adsorbed with H were considered



Scheme 1. Reaction pathways and surface species during temperature increase following acetic acid adsorption on a highly reduced (lower) and a fully oxidized (upper) CeO₂ surface.

using DFT, including acetate/ V_0 with H (Fig. 10D) and acetate/ VV_0 with H (Fig. 10F). For these structures, the computed modes correspond to the methyl rock near 1010 cm⁻¹, the $v_s(OCO)$ and $v_a(OCO)$ fall in the range of 1310–1390 cm⁻¹ while the CH₃ scissor mode falls in the range 1410–1440 cm⁻¹. Qualitatively these features are also consistent with the main features observed at 1050, 1330, 1396, and 1430 cm⁻¹ at 444 K (Fig. 7). Two other partly dehydrogenated states described as surface ketene intermediate (CH₂=COO) adsorbed at a single oxygen vacancy (Fig. 10G) or an oxygen vacancy dimer (Fig. 10H) were also considered. The simulated IR spectra for these structures do not contain any strong IR mode and are omitted from Fig. 11.

Two factors should be noted. First, the DFT spectra suggest that the peak positions are affected by neighboring acetate and H, for example compare μ -acetate and μ -acetate + H in Fig. 11A. There may be many other similar local arrangements involving µ-acetate, acetate in vacancies, and H that are frozen at low temperatures but evolve as temperature is raised, and these can lead to shifting and broadening of the peaks. Second, the DFT-calculated peaks are generally red-shifted compared to experiments, as has been reported RAIRS studies of formic acid adsorption on ceria [13,14]. Taking these two factors into consideration, the RAIRS spectra and calculated IR spectra suggest that μ -acetate and acetate/ V_o coexist on the oxidized surface and that acetate is predominantly adsorbed in oxygen vacancies on the reduced surface.

The observed reaction products that desorb above 500 K are the result of the transformations occurring on the CeO₂ surface. Two major reaction pathways open up and compete as the temperature is increased above 500 K. They are unimolecular dehydration to form ketene:

$$CH_3COOH \rightarrow CH_2 = C = O + H_2O \tag{1}$$

and the bimolecular coupling reaction to form acetone:

$$2CH_3COOH \rightarrow (CH_3)_2C=0 + CO_2 + H_2O$$
 (2)

Except for acetic acid, ketene and acetone are the main multiple C containing products observed for the initially oxidized surface and ketene is favored over acetone. These balanced reactions do not describe the pathways that occur during the TPD, since the low-temperature water evolution and the formation of acetate are indications of stepwise processes of deprotonation to an intermediate. Acetone formation implies reaction between two deprotonated acetates with methyl transfer from one to the other, thereby forming COO- that leads to subsequent release of CO₂:

$$CH_3COO - + CH_3COO/V_0 \rightarrow (CH_3)_2C = 0 + COO -$$
(3)

The CO₂ TPD product correlates reasonably with the acetone as expected from Eq. (3). Specifically, on the initially oxidized surface the acetone slightly precedes the (larger) CO_2 production (Fig. 1), while on the highly reduced surface both acetone formation and CO₂ formation are eliminated (Fig. 2). Although acetone production yields CO₂ it is possible that CO₂ may also result from unimolecular decomposition of acetate. It is of mechanistic importance that for the oxidized surface ketene and acetone are both evolved at nearly the same temperature (600 K) with the same TPD peak signature, although acetone is smaller. This coincidence suggests formation of surface ketene may be rate-limiting the formation of acetone.

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G Model

Under UHV conditions the unimolecular formation of ketene may be favored over acetone simply because the coupling reaction is bimolecular and less favored as coverage decreases during TPD. Although acetate reacts by these routes during TPD in UHV leaving a clean surface (for the initially oxidized surface) or a surface with carbon residue (for the initially reduced surface), the acetates are stable up to almost 550 K. These results are therefore consistent with the observation that bulk cerium acetate forms during steady state reaction of acetic acid below 300 °C (573 K).[9]

Evidence for both of the net reactions (1) and (2) have been reported previously on $CeO_2(111)$ and $CeO_2(100)$ surfaces, where low temperature acetic acid adsorption led to the evolution of ketene and a lesser amount of acetone during TPD [51]. However, the effect of surface reduction upon the acetone:ketene selectivity that is evident here was not previously reported. Similarly Barteau and Kim [50] examined room temperature acetic acid adsorption on TiO₂ powders (anatase) and found acetone and ketene production consistent with these reactions. However, they found that acetone was favored over ketene, indicating altered selectivity compared to CeO₂ where acetone production is smaller. On TiO₂ the CO₂ production lagged the acetone production slightly in TPD and was in comparable yields to the acetone production.

Pestman et al. [57,58] studied the temperature-programmed reaction of several acids on various oxide catalysts as a route to ketone formation. For reactions of acetic acid, acetone was the primary product although they also found ketene and they examined how its formation depends upon oxide and reaction conditions. Interestingly, they proposed a flat-bonded "ketene-like" intermediate for the formation of acetone from acetic acid. Their evidence was based upon comparison of aldehyde:ketone selectivity of several acids with or without available α -H (i.e. H covalently bonded to the C adjacent to the carboxylate carbon). Our TPD indicates that ketonization to acetone is observed in small amounts from the oxidized surface although it decreases on the more highly reduced surfaces (Fig. 3). The acetate/ V_0 state observed at low temperatures when vacancies are present, which is equivalent to a stably bonded acetyl, could be an intermediate that is thermally activated to yield both the observed desorption of ketene and the acetone ketonization product. Evolution of ketene first requires the thermally activated loss of the α -H to form a ketene-like intermediate CH₂=COO/V₀ where one of the oxygens is strongly bonded at a vacancy site (Fig. 10G), followed by the cleavage of the C–O bond. This intermediate can also be viewed as a bent ketene bonded to a surface O via the carboxyl C. Its C–C bond has a length of 1.382 Å, which falls in the C=C double bond range [7], and is -1.09 eV with respect to gas-phase ketene. Based upon the DFT adsorption energy, it is likely that upon the loss of the α -H in the acetate/V_o state at elevated temperatures, the CH2=COO intermediate rapidly undergoes C-O bond cleavage to release ketene. Linear ketene is calculated not to adsorb on $CeO_2(111)$.

Experimentally there is faint spectroscopic evidence for stably adsorbed ketene. In sXPS, a carbonyl bond of ketene should be apparent at a binding energy between the carboxyl and the methyl peaks. No such peak is evident in this range on the initially oxidized surface (Fig. 4B) although on the initially reduced surface a weak broad shoulder is observed at the higher annealing temperatures (Fig. 6B). However, the reduced surface exhibits less ketene desorption than the oxidized surface, contradicting the hypothesis that the peak is due to ketene. Also, the binding energy of the shoulder feature is more closely positioned to be enolate than ketene. DFT suggests that the ketene vibrational modes, being very weak, would be difficult to see in RAIRS so failure to see them is inconclusive. The NEXAFS resonance assigned to π^* (C=C) is compelling evidence for a carbon-carbon double bond. But the resonance is also seen more intensely on the initially reduced surface than the oxidized surface, opposite to the trend of ketene desorption. These resonances could

also be due to enolate or carbonaceous residue. Enolate formed from acetaldehyde has been observed on $CeO_2(111)$ by RAIRS and is characterized by peaks near 1194 and 1600 cm⁻¹ [7] and such features are not seen clearly in the RAIRS data for either oxidized or reduced ceria (Figs. 7 and 8). Enolate would be a natural precursor to the small amount of acetaldehyde desorption that is observed from the reduced surface. Therefore, we conclude that acetate/V₀ is the precursor to ketene, which is rapidly desorbed upon formation (and so not observed spectroscopically) and that enolate in small amounts is likely leading not to ketene but to acetaldehyde.

The present studies demonstrate that the TPD product distribution is quite different when the initial surface is highly reduced. Differences are shown from comparison of Figs. 1 and 2 and summarized in Fig. 3 and Scheme 1. Briefly, highly reduced surfaces lead to much more reduced products, a natural result of reoxidation of the surface by the acetic acid. Consistent with this expectation is that the ratio of H₂:H₂O is greatly increased on the reduced surface compared to the oxidized surface, as is the ratio of CO:CO₂. There is a decrease of ketene but an increase in acetaldehyde and acetylene resulting from unidentified, partially dehydrogenated intermediates. Reduction of the surface shuts down the coupling reaction probably because of rapid deoxygenation of the acetate intermediates. This variation in the TPD product distribution is accompanied by a variation in extent of reduction of the oxide surface. Adsorption of acetic acid reduces a fully oxidized surface in part by providing free H that reacts with the surface to evolve as water at low temperature, but acetic acid also oxidizes a highly reduced surface by leaving O on the surface. This behavior is similar to that reported previously for formic acid [59] Another effect of a highly reduced surface is that carbonaceous residue remains at high temperature on the reduced surface for lack of available O. Finally, the fact that the yield of acetone decreases on the more reduced surface suggests that acetate/V_o is not sufficient for the formation of acetone or even ketene, since both products decrease as the surface becomes highly reduced. Formation of acetylene outcompetes ketene desorption on the reduced surface, while the decrease in µ-acetate on reduced surface inhibits acetone formation. A practical implication is that catalytic selectivity from a reactor may be adjusted by controlling the reducibility of the reactant stream, for example by co-feeding H₂ or water.

5. Conclusions

Adsorption and transformations of acetic acid were studied upon a model $CeO_2(111)$ surface. Near 175 K acetic acid adsorbs to form a mix of molecular acetic acid and deprotonated acetate. Acetic acid desorbs at low temperature along with water that leads to reduction of the CeO₂ surface. The resulting oxygen vacancies form strong adsorption sites that trap acetate. Adsorbate states are best described by a mixture of bridge bonded µ-acetate and acetate bonded at an oxygen vacancy (acetate/ V_0), and a small amount of enolate observed primarily on the more reduced surfaces. At temperatures near 500-600 K products competitively desorb in a mix of acetic acid, ketene, acetylene and acetone. Acetate/V₀ is the precursor to ketene and to acetylene, and its reaction with µ-acetate leads to acetone. UHV conditions favor the unimolecular product (ketene) over the coupling product (acetone) during TPD. At higher temperature further decomposition to form CO and CO₂ is observed. The distribution of desorption products is strongly dependent upon the extent of reduction of the surface prior to adsorption. Increased reduction increases the ratio of H₂:H₂O and the ratio of CO:CO₂, and favors formation of acetaldehyde compared to acetone or ketene. It is suggested that in a catalytic reactor, the selectivity for acetone by ketonization of acetic acid should be sensitive to co-fed reducing or oxidizing gases in the reactor stream.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2015.03. 033

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