

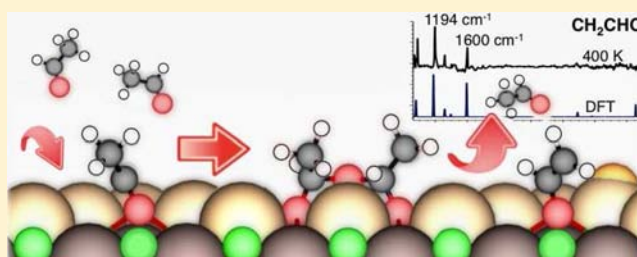
Oxygen Vacancy-Assisted Coupling and Enolization of Acetaldehyde on CeO₂(111)

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S Supporting Information

ABSTRACT: The temperature-dependent adsorption and reaction of acetaldehyde (CH₃CHO) on a fully oxidized and a highly reduced thin-film CeO₂(111) surface have been investigated using a combination of reflection–absorption infrared spectroscopy (RAIRS) and periodic density functional theory (DFT+U) calculations. On the fully oxidized surface, acetaldehyde adsorbs weakly through its carbonyl O interacting with a lattice Ce⁴⁺ cation in the η¹-O configuration. This state desorbs at 210 K without reaction. On the highly reduced surface, new vibrational signatures appear below 220 K. They are identified by RAIRS and DFT as a dimer state formed from the coupling of the carbonyl O and the acyl C of two acetaldehyde molecules. This dimer state remains up to 400 K before decomposing to produce another distinct set of vibrational signatures, which are identified as the enolate form of acetaldehyde (CH₂CHO⁻). Furthermore, the calculated activation barriers for the coupling of acetaldehyde, the decomposition of the dimer state, and the recombinative desorption of enolate and H as acetaldehyde are in good agreement with previously reported TPD results for acetaldehyde adsorbed on reduced CeO₂(111) [Chen et al. *J. Phys. Chem. C* **2011**, *115*, 3385]. The present findings demonstrate that surface oxygen vacancies alter the reactivity of the CeO₂(111) surface and play a crucial role in stabilizing and activating acetaldehyde for coupling reactions.



1. INTRODUCTION

Aldehydes and ketones are two major types of oxygenate obtained in the thermochemical processing of solid biomass.^{1,2} Those that contain hydrogen on the carbon adjacent, or α , to the carbonyl group can undergo C–C coupling reactions, including aldol condensation and Michael addition, to produce longer carbon chains,^{3–5} providing a route by which oxygenates derived from solid biomass can be converted into fuel-range hydrocarbons.^{6,7} It is well-known that these coupling reactions take place through enolate intermediates, formed via α -H abstraction, and that the formation of enolates can be catalyzed either by an acid or by a base. In addition, enolates have been identified as the intermediates in halogenation, alkylation, and coupling reactions.³

There has been interest in developing bifunctional heterogeneous catalysts for these reactions⁸ because of the need for cost-effective, environmentally friendly technologies for the conversion of biomass into fuels and for the production of chemicals. Solid acid and base catalysts have been used successfully for aldol condensation, and the role of acid–base bifunctionality has been emphasized by previous workers.^{9–11} For Michael addition and Knoevenagel condensation, solid catalysts with highly basic character have been used successfully.^{12–17} Heterogeneously catalyzed aldol condensation of acetaldehyde to crotonaldehyde has been reported on uranium oxide,¹⁸ TiO₂,^{5,19–22} MgO/SiO₂ and ZrO₂/SiO₂,²³ zeolites,²⁴ CeO₂,²⁵ and metals supported on metal oxides.^{25–27}

To better understand how such solid catalysts for C–C coupling reactions work, it is instructive to understand the molecular pathways by which a model aldehyde, e.g., acetaldehyde (AcH), interacts with catalytic oxides. The keto–enol tautomers AcH and vinyl alcohol are close in energy,²⁸ and either form might be expected to be stabilized on an oxide surface. The enolate anion of acetone has been identified on oxides^{29,30} and metal surfaces.³¹ There have also been reports of enolates forming from the reactions of AcH on Co/Al₂O₃³² and from the oxidation of alcohols by NO on Ag/Al₂O₃.³³ The aldol addition product of AcH, 3-hydroxybutanal, has been spectroscopically observed upon acetaldehyde adsorption on TiO₂.⁵ Here we focus on CeO₂ (ceria) as an example, an oxide that can impart synergistic activity to metal catalysts and is catalytically active in its own right. Although coupling products including crotonaldehyde and crotyl alcohol have been reported in the TPD of AcH on ceria powder²⁵ and surface reaction intermediates have been observed on ceria surfaces,³⁴ the mechanistic aspects of AcH reactivity, including the enolization of AcH, remain unclear. In the case of a reducible oxide such as ceria, it is furthermore of fundamental interest to understand the role of oxygen vacancies in the keto–enol tautomerization and coupling reactions of AcH.

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Table 1. Experimental and Calculated Values of IR-Active Vibrations (in cm^{-1}) for Acetaldehyde

assignment	gaseous AcH		solid AcH	multilayer on $\text{CeO}_2(111)$	satd adsorbed layer on $\text{CeO}_2(111)$	1/2 ML ($\eta^1\text{-O}$) on $\text{CeO}_2(111)$	satd layer on Ni(111)
	ref 65	present work (DFT)	ref 61	present work	present work	present work (DFT)	ref 63
$\nu_{\text{as}}(\text{CH}_3)$ a'	3005	3088	3003	3002	3065	3074	3005
$\nu_{\text{as}}(\text{CH}_3)$ a	2967	3021	2964	2970		3019	
$\nu_{\text{s}}(\text{CH}_3)$ a'		2959	2918	2918	2965	2963	
$2\nu_6$ Fer Res $\nu_{\text{s}}(\text{CH}_3)$ a'			2840 2850	2855			
$\nu(\text{CH})$ a'	2822	2795	2716–2750	2760–2746	2856	2864	
$\nu(\text{C}=\text{O})$ a'	1743	1752	1718–1703	1723	1708	1712	1670
$\delta_{\text{as}}(\text{CH}_3)$ a'	1441	1418	1429	1426			
$\delta_{\text{as}}(\text{CH}_3)$ a	1420	1415	1406		1410	1407	
$\delta(\text{CH})$ a'	1400	1376	1391	1391	1370	1358	1393
$\delta_{\text{s}}(\text{CH}_3)$ a'	1352	1324	1350	1350	1351	1317	1347
$\nu(\text{CC})$ a' (+ $\rho(\text{CH}_3)$)	1113	1097 1088	1119	1122	1109–1143	1092	1129
$\nu(\text{C}-\text{O})$					1046 ^a		
$\rho(\text{CH}_3)$ a'	919		920				
$\rho(\text{CH}_3)$ a + $\nu(\text{CC})$	867	871	867			879	
$\gamma(\text{CH})$ a	763	740	764			757	

^aEthoxide impurities or $\mu\text{-C}_2\text{O}$ AcH.

Previously Chen and Mullins investigated the adsorption of AcH on a fully oxidized and a highly reduced thin film $\text{CeO}_2(111)$ surfaces by a combination of temperature-programmed desorption (TPD), soft X-ray photoelectron spectroscopy (sXPS), and near-edge X-ray absorption fine structure (NEXAFS).³⁴ From TPD it was found that AcH adsorbs weakly on the fully oxidized $\text{CeO}_2(111)$ surface and that the physisorbed multilayer AcH desorbs below 175 K leaving a chemisorbed layer, which in turn desorbs intact with a peak desorption temperature at 210 K. On a highly reduced surface (60% Ce^{3+}) AcH adsorbs strongly and desorbs in two clearly resolved states in TPD at 400 K and 550–600 K. sXPS suggested that the remaining surface species is a carbanion interacting through the methyl group with a surface Ce^{4+} . The higher temperature wave is accompanied by C_2 hydrocarbons, ethylene and acetylene, indicating partial decomposition of the adsorbate.

In the present work, we investigate this system using a combination of reflection absorption infrared spectroscopy (RAIRS) and density functional theory (DFT) calculations. The measured IR spectra are compared with the DFT-calculated IR spectra to determine the nature of the dominant surface species at different temperatures, and the energetics of the surface species are calculated to provide a direct link to the previous TPD results. Together the previous TPD, XPS, and NEXAFS results and the current RAIRS and DFT findings thus establish the temperature-dependent reaction pathways of AcH on the $\text{CeO}_2(111)$ crystalline facet. It is found that weak chemisorption of AcH in the molecular (keto) form dominates on the fully oxidized surface, but the presence of oxygen vacancies produces richer chemistry, including the formation of the enolate (CH_2CHO^-) from AcH. Interestingly, no aldol addition product is detected despite enolate formation, and instead, a C–O coupling species formed from two AcH molecules is seen as a major surface intermediate. The role of oxygen vacancies and the factors that disfavor aldol addition are discussed, shedding light on what would be needed to enable desired coupling reactions on the (111) and possibly other facets of ceria.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

Experiments were performed in an ultrahigh vacuum (UHV) chamber described previously.³⁵ Thin CeO_2 films were deposited onto the Ru(0001) single crystal substrate following methods described previously.³⁶ By these methods, reproducible flat surfaces of CeO_2 oriented with the (111) face exposed were obtained. Ce metal was evaporated onto the Ru crystal held at 700 K in the presence of O_2 . By varying the O_2 pressure, surfaces with different ratios of $\text{Ce}^{3+}/\text{Ce}^{4+}$ could be obtained to study the influence of Ce oxidation state and oxygen vacancies. After finalizing the CeO_2 deposition and before the adsorption of AcH, the sample was annealed at 900 K for at least 10 min to ensure the distribution of vacancies was uniform throughout the entire film. The reduced surface contained 60% Ce^{3+} as determined by XPS. Throughout this paper the reduced surface is referred to as $\text{CeO}_{2-x}(111)$. AcH (Aldrich, >99.0% pure) was outgassed using several freeze–pump–thaw cycles and dosed onto the surface through a variable leak valve.

RAIRS measurements were acquired in a UHV chamber where the model catalyst was prepared and characterized by X-ray photoelectron spectroscopy (XPS). This system has the capabilities to clean the sample and check gas purity (Ar ion sputtering, mass spectrometry). Appended to the UHV chamber, there is a differentially pumped RAIRS cell into which the Ru(0001) substrate is translated using a long-travel manipulator. The sample substrate is mounted between two 0.1 mm W wires connected to support rods and is resistively heated through the mounting wires. Sample temperature is measured using a type-K thermocouple spot-welded to the side of the Ru substrate, and the temperature can be controlled between 90 and 1000 K. RAIRS was performed 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. The RAIRS cell is pumped using a turbo-molecular pump that holds a base pressure of $1\text{--}2 \times 10^{-9}$ Torr. The IR beam was passed through differentially pumped CaF_2 windows into the RAIRS cell, and the beam path external to the RAIRS cell was purged by dry air. All spectra shown below are differences between the IR absorption spectrum at a certain condition and a reference spectrum recorded for the clean ceria surface. Due to limitations in IR transmission and sensitivity, only absorption above about 1000 cm^{-1} are reliable and reported here. To minimize thermal artifacts, temperature effects were studied by heating the sample to the temperature of interest and then allowing it to cool to the reference temperature. All spectra were collected at an instrumental resolution of 4 cm^{-1} and the signal

averaged for 1024 scans. The temperatures at which the RAIRS spectra were collected were chosen in view of the different desorption spectra reported in the previous TPD study,³⁴ as summarized above.

Periodic, spin-polarized DFT calculations were performed within the generalized gradient approximation (GGA-PW91)³⁷ using the Vienna Ab initio Simulation Package (VASP).^{38–40} The core electrons were described by the projector-augmented wave method (PAW),⁴¹ 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 (2 × 2) surface unit cells, which corresponds to 1/4 monolayer (ML) of coverage for each adsorbate per unit cell. The exact structure of the reduced CeO_{2-x}(111) surface is not known. We used a point oxygen vacancy (denoted V_o) in the surface of the CeO₂(111) slab (also at 1/4 ML coverage) to model the CeO_{2-x}(111) surface, which, as our previous DFT study of formate adsorption on ceria³⁵ and the current results show, is able to effectively capture the vibrational properties of oxygenated species on the reduced surface.

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 decoupling⁴² in the z direction. The surface Brillouin zone was sampled with a 2 × 2 × 1 Monkhorst–Pack k-point grid.⁴³ Geometry optimization was converged to below 0.01 eV/Å in each degree of freedom for all relaxed atoms.

The vibrational frequencies and simulated IR spectra of surface adsorbates were calculated using the Atomic Simulation Environment.⁴⁴ 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.⁴⁵ 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. As an indication of the accuracy of these calculations, the vibrational modes and frequencies for an isolated gas-phase AcH molecule were calculated and compared with the experimental gas-phase reference measurements in Table 1.

The adsorption energy was calculated as $\Delta E = (E_{\text{total}} + E_{\text{total}}^{\text{ZPE}}) - E_{\text{slab}} - (E_{\text{mol}} + E_{\text{mol}}^{\text{ZPE}})$, 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 alone in the gas phase in a neutral state (closed-shell or radical). The zero point energies (E^{ZPE}) were calculated from the vibrational frequencies (ν_i) of an adsorbate molecule as $E^{\text{ZPE}} = 1/2 \sum_i h\nu_i$. A more negative ΔE therefore corresponds to stronger adsorption. The minimum-energy reaction path for an elementary step and the transition state (TS) associated with it were determined using a combination of the climbing-image nudged elastic band method⁴⁶ and the dimer method.⁴⁷ The activation energy was calculated as $E_a = (E_{\text{TS}} + E_{\text{TS}}^{\text{ZPE}}) - (E_{\text{IS}} + E_{\text{IS}}^{\text{ZPE}})$, where IS denotes the initial state. Each TS was verified to possess only one imaginary mode in the direction of the bond breaking or forming process. Different spin states were calculated, and the lowest adsorption energy was reported for each adsorbate.

DFT at the GGA level fails to properly describe the localization of the Ce 4f electrons that occurs with the reduction of Ce⁴⁺ to Ce³⁺ due to strong interaction among f electrons.⁴⁸ To compensate for this deficiency, the DFT+U formalism of Dudarev et al.⁴⁹ 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 Ce₂O₃ and in oxygen vacancies in CeO₂, although no single value of U can simultaneously improve the predictions for all properties of bulk CeO₂ and Ce₂O₃.^{50,51} Nonetheless, the method has been productively applied to a number of theoretical investigations of chemistry on CeO₂ surfaces.^{35,52–55} With a judicious choice of the U value, the DFT+U method has been shown to perform on par with hybrid functionals in predicting the relative spin-state energetics of transition metal species.⁵⁶ In keeping with our previous study on formate adsorption on CeO₂(111) surfaces,³⁵ U = 0, 2, and 5 eV were

used in this study because these values offer a range of values from one that is suitable for reaction energetics (U = 2), to one that is suitable for localizing f electrons in Ce³⁺ (U = 5), to no DFT+U (U = 0).^{50,51} The lattice constant of bulk CeO₂ was calculated on a 15 × 15 × 15 k-point grid to be 5.468, 5.476, and 5.494 Å for U = 0, 2, and 5 eV, which compare closely with the experimental value of 5.41 Å. For the sake of brevity, most results discussed below were obtained for U = 2 eV, but several key energetic and vibrational quantities were calculated at U = 0 and 5 eV and are compared with the corresponding values for U = 2 eV. Bader charge partition analysis was performed using the approach of Henkelman.⁵⁷

3. RESULTS

3.1. Acetaldehyde on CeO₂(111). Figure 1 shows the RAIRS spectrum of a multilayer obtained by dosing AcH at 100

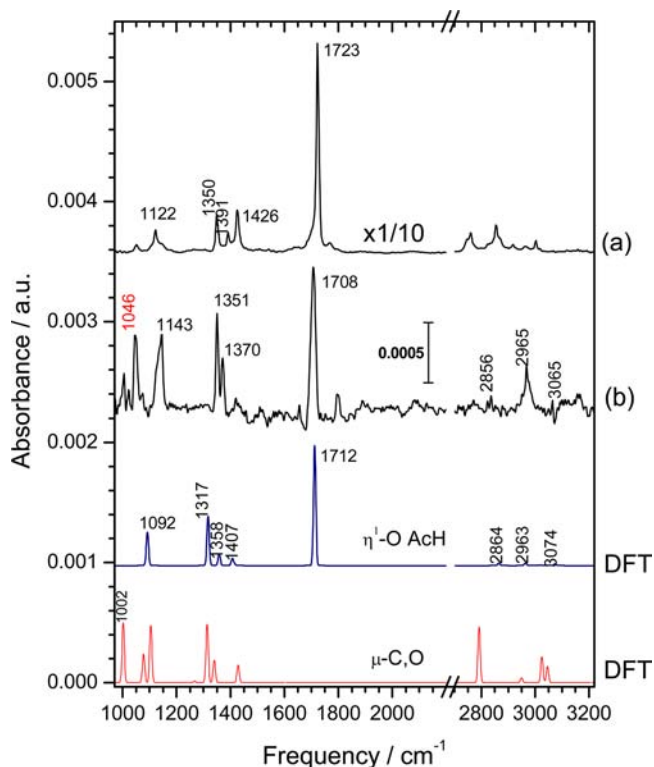


Figure 1. RAIRS spectra are shown for acetaldehyde adsorbed on fully oxidized CeO₂(111) for multilayer adsorbed at 100 K (curve a) and a saturation monolayer adsorbed at 175 K (curve b). The DFT-calculated spectra are shown for 1/2 ML η^1 -O AcH and for 1/4 ML μ -C₂O AcH.

K (curve a) and of a saturation layer of AcH adsorbed on CeO₂(111) at 175 K (curve b). The exact coverage of the saturation layer cannot be determined at present. All of the vibrational features detected in the multilayer spectrum correspond well to gas phase acetaldehyde, and their assignments are presented in Table 1 together with reference data. The features in the saturated layer roughly correspond to the multilayer feature but with frequency shifts showing that the molecule is intact but interacting with the surface. All vibrational features detected in the saturated layer are assigned following previous literature.^{58–65} Prominent in the RAIRS spectrum is a feature at 1723 cm⁻¹ that is the hallmark of a carbonyl group on the surface. When the saturation layer is heated to 210 K and above, the molecules completely desorb as AcH, in agreement with the previous TPD experiments.³⁴

The DFT-calculated minimum-energy adsorption geometry for AcH on CeO₂ (111) is shown in Figure 2a. AcH adsorbs weakly through its carbonyl oxygen on the top of a Ce⁴⁺ cation in the surface trilayer. The preferred geometry involves the C=O bond oriented at an angle from the surface normal so that the acyl H atom approaches a surface lattice O atom. This is the η^1 -O configuration that has been reported in the literature for AcH^{60,63,66} and acetone⁶⁷ adsorption on oxides and metals. Interaction between the acyl H and the lattice O²⁻ anion may help orient this configuration. The adsorption energy (ΔE) of this state is -0.21 and -0.09 eV at 1/4 and 1/2 ML coverages, respectively (Table 2). At 1/2 ML, the calculated C=O and C–C bond lengths are $d_{C-O} = 1.227$ Å and $d_{C-C} = 1.497$ Å, nearly identical to those of the calculated gas-phase acetaldehyde molecule ($d_{C-O} = 1.219$ Å and $d_{C-C} = 1.498$ Å; Table 2), a further indication of weak interaction with the surface. The C=O bond is at $\alpha = 55^\circ$ from the surface normal.

The calculated spectrum for the η^1 -O state at 1/2 ML is shown in Figure 1c, with the principal vibrational frequencies and assignments listed in Table 1. There is close agreement between the calculated spectrum and the experimental spectrum for the saturation layer (Figure 1b). The most intense feature in the calculated spectrum is the carbonyl stretch at 1712 cm⁻¹, in good agreement with the strong feature observed for the saturation layer at 1708 cm⁻¹. The observed carbonyl stretch is slightly red-shifted from its value in the multilayer indicating that the carbonyl oxygen interacts weakly with the surface. For comparison, AcH interaction with metals can be stronger.^{60,63,66,68,69} On both Ni(111)⁶³ and Ru(0001)⁶⁶ the molecule adsorbs in the η^1 -O configuration at certain coverages and the observed C=O stretch is red-shifted considerably to 1670 cm⁻¹ (the findings on Ni(111) are listed in Table 1 for comparison).

In the C–H stretching region (2600 – 3200 cm⁻¹), a sharp peak at 2965 cm⁻¹ and a weak peak at 2856 cm⁻¹ are seen experimentally (Figure 1b). On the basis of comparison with solid AcH, the peak observed at 2965 cm⁻¹ is assigned to a methyl stretch, which confirms that the methyl group is intact. The calculated spectrum exhibits peaks at 3074 , 3019 (weak), and 2963 cm⁻¹ that are due to C–H stretches of the methyl group. The peak at 2963 cm⁻¹ corresponds to a symmetric stretch and suggests that the experimentally observed peak at 2965 cm⁻¹ is due to the symmetric stretch. DFT also predicts a peak at 2864 cm⁻¹ due to the C–H stretch of the acyl H, which corresponds to the weak feature seen experimentally at 2856 cm⁻¹.

In the skeletal region (1500 – 1000 cm⁻¹) the assignments are not straightforward because of the coupling of modes and Coriolis interactions in this region.^{61,62} A group of modes are calculated to be located between 1300 and 1450 cm⁻¹ with the two most intense modes being 1317 and 1358 cm⁻¹. These correspond well to the two main features seen in the experimental spectrum at 1351 and 1370 cm⁻¹ (Figure 1b), and so these features are assigned to $\delta_s(\text{CH}_3)$ and $\delta(\text{CH})$ bending modes, respectively. For the region below 1200 cm⁻¹, the experimental spectrum shows a broad feature with a peak at 1143 cm⁻¹ and a shoulder at 1109 cm⁻¹. In the literature this feature has been assigned to a C–C stretch but with contribution from rocking modes of the methyl group.^{60,61,63,68} Our calculations indicate an intense mode at 1092 cm⁻¹ that corresponds to a methyl rock and C–C stretch with a change in the dipole moment perpendicular to the surface, consistent with the η^1 -O state (Figure 2a). The peak at

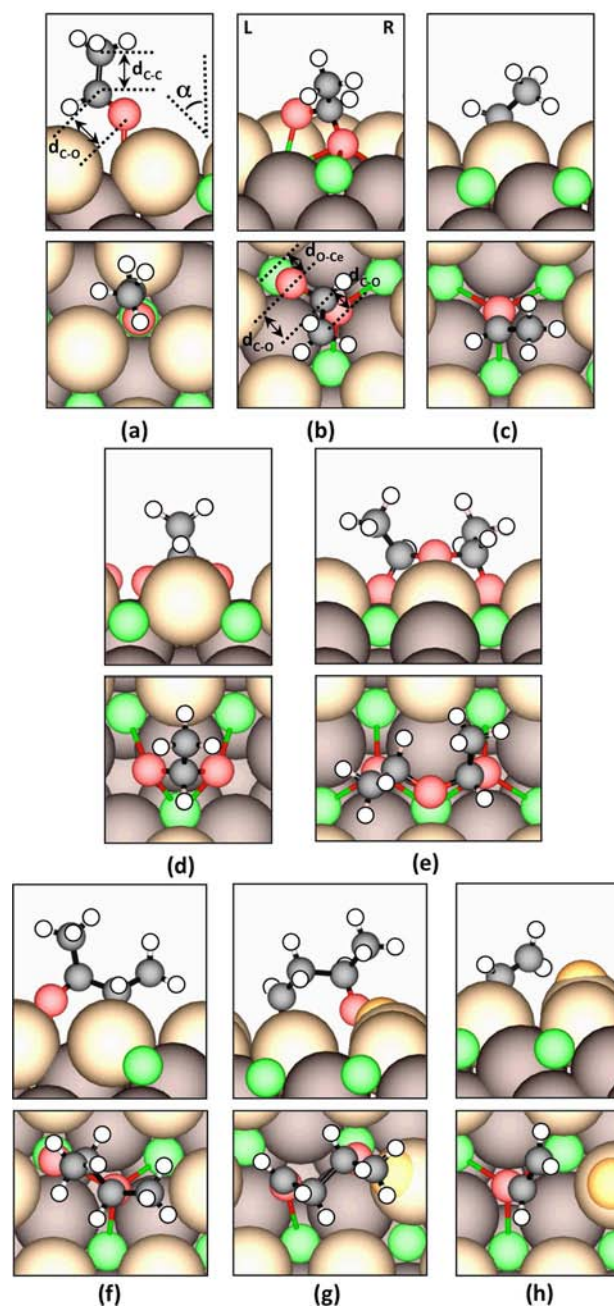


Figure 2. DFT-calculated minimum-energy structures for various surface states of acetaldehyde on CeO₂(111). Without a surface oxygen vacancy: (a) AcH (η^1 -O); (b) AcH (μ -C,O). With a surface oxygen vacancy: (c) AcH/ V_o ; (d) dioxy (1,1-dioxyethane); (e) 1,1'-oxydiethoxide (C–O dimerized AcH); (f) 2,3-butanediolate (C–C dimerized AcH); (g) 3-oxybutanal + H (C–C dimerized AcH); (h) enolate/ V_o +H. In each panel side view is on top and top view is on bottom. 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 slightly lighter to be distinguished from lower-layer lattice O atoms. Medium orange spheres in panels g and h represent dissociated H atoms that form co-adsorbed surface hydroxyl groups. Bonds between O in AcH and lattice Ce are for illustrative purposes only. The definitions of bond lengths (d) and tilt angle of the C=O bond (α) are indicated in panels a and b. “L” and “R” are illustrated in panel b to facilitate the identification of multiple bonds and atoms in Table 2. Molecular images are made using VESTA.⁹⁹

Table 2. DFT-Calculated Adsorption Energy (ΔE ; in eV/AcH; Relative to Gas-Phase AcH; Zero Point Energy-Corrected); Zero Point Energy (ZPE; in eV); C–O and C–C Bond Lengths ($d_{\text{C-O}}$ and $d_{\text{C-C}}$; in Å); Magnetic Moment; and Bader Charge on the Acyl C atom (e) for Optimized Structures of the Various Surface States of AcH Shown in Figure 2^a

	ΔE	ZPE	$d_{\text{C-O}}$	$d_{\text{C-C}}$	magnetic moment	Bader charge
Adsorbed Ach States						
AcH ($\eta^1\text{-O}$) ^b	−0.20	1.51	1.225	1.493	0	+0.86
(with vdW)	−0.48	1.51	1.230	1.494	0	+0.90
AcH ($\eta^1\text{-O}$, 1/2 ML)	−0.09	1.51	1.227	1.497	0	+0.90
AcH ($\mu\text{-C,O}$) ^b	−0.53	1.57	1.375	1.523	0	+0.97
			1.458			
AcH/ V_{o}	−1.09	1.53	1.304	1.485	2	+0.51
dioxy	−0.95	1.63	1.455	1.521	2	+0.89
			1.443			
1,1'-oxydiethoxide (C–O dimerized)	−1.24	3.25	1.398	1.518	2	+0.91
			1.470	1.522		+0.88
			1.481			
			1.400			
2,3-butanediolate (C–C dimerized)	−1.22	3.19	1.400	1.532	0	+0.52
			1.443	1.544		+0.44
				1.526		
3-oxybutanal ^c (C–C dimerized)	−0.92	3.17	1.259	1.451	2	+0.78
			1.362	1.628		+0.61
				1.535		
enolate/ V_{o} ^c	−1.86	1.55	1.350	1.350	2	+0.37 ^e
Gas-Phase Species						
AcH			1.219	1.498	0	+0.95
vinyl alcohol	+0.45 ^d		1.374	1.332	0	
ethanol			1.433	1.512	0	
diethyl ether			1.425	1.513	0	
ethylene				1.331	0	

^aResults are calculated at $U = 2$ eV and coverage of 1/4 ML except where noted. ΔE for 1/2 ML and coupled states is averaged over two AcH. When more than one C–O or C–C bond or more than one acyl C atom exists, the values are listed in the order of appearance from left to right in the corresponding figures in Figure 2, as illustrated in Figure 2b. Calculated gas-phase molecules are included for comparison of bond lengths. ^bThe distance between the carbonyl O and the nearest Ce is 2.689 Å for $\eta^1\text{-O}$; 2.637 Å for $\eta^1\text{-O}$ with vdW-DF; 2.212 Å for $\mu\text{-C,O}$; and 2.376 Å bulk CeO_2 . ^cDenotes that the state includes a dissociated hydrogen in the form of a co-adsorbed surface hydroxyl. ^dRelative to gas-phase AcH. ^eBader charge on the methylene C is $-0.10 e$.

1046 cm^{-1} is considered to be the C–O stretching mode of an ethoxy impurity.⁷⁰ Its intensity was small compared to that measured for an adsorbed ethoxide layer, and was found to be variable relative to the AcH features, consistent with its being due to a sporadic impurity.

To further confirm these assignments, experiments were done in the same conditions as in Figure 1 using perdeuterated AcH ($\text{AcH-}d_4$) and the results are presented in the Supporting Information section (Supplementary Figure S1) together with reference data from literature and our DFT-calculated results. The perdeuterated results further support that AcH is adsorbed on $\text{CeO}_2(111)$ in the $\eta^1\text{-O}$ state.

It has been previously reported that formaldehyde adsorbs on $\text{CeO}_2(111)$ and on other oxides by forming a bond between the acyl C and a lattice O and another bond between the carbonyl O and a Ce^{4+} cation, to form a $\mu\text{-C,O}$ configuration (also termed the η^2 state in early literature).^{71,72} Therefore we also optimized the $\mu\text{-C,O}$ AcH state on $\text{CeO}_2(111)$ (Figure 2b). It is somewhat more stable than the $\eta^1\text{-O}$ state (Table 2). The main vibrational features of the $\mu\text{-C,O}$ state (Figure 1d) include one (1002 cm^{-1}) that possibly corresponds to the 1046 cm^{-1} peak observed experimentally (Figure 1b), with the remaining peaks difficult to be distinguished from that of the $\eta^1\text{-O}$ state. Therefore the possibility that the $\mu\text{-C,O}$ state is present on the surface cannot be completely eliminated.

However, the prominent carbonyl peak seen in Figure 1 clearly indicates that the majority of the AcH is in the $\eta^1\text{-O}$ state.

3.2. Acetaldehyde on $\text{CeO}_{2-x}(111)$. Acetaldehyde was adsorbed at 175 K on the reduced $\text{CeO}_{2-x}(111)$ surface (60% Ce^{3+}) following the same procedures as in the case of the fully oxidized $\text{CeO}_2(111)$ surface. Spectra were recorded at 100 K after annealing to various temperatures from 175 to 400 K. Below 220 K the most readily identifiable peak in the RAIRS spectra (not shown) is the C=O peak at 1708 cm^{-1} , due to the $\eta^1\text{-O}$ AcH adsorbed on the oxidized portions of the surface, but it is accompanied by other features associated with the reduced sites. Upon heating above 220 K, the peaks associated with the $\eta^1\text{-O}$ AcH disappear, while those associated with the reduced sites remain. Figure 3 (top curve) shows the RAIRS spectrum after heating to 300 K. It can be seen that the C=O feature near 1700 cm^{-1} is absent, which implies that either the surface species does not contain a carbonyl group or the C=O bond axis lies parallel to the surface and cannot be detected by RAIRS. In addition, there is a clear feature at 2978 cm^{-1} in the C–H_x stretching region that may be a $\nu_s(\text{CH}_3)$ mode, implying that the methyl group is still intact. The remaining features observed in the RAIRS spectrum include a peak at 1383 cm^{-1} that may be a CH_x deformation mode, a more intense feature at 1134 cm^{-1} , and weaker features at 1061 and 976 cm^{-1} . Finally a

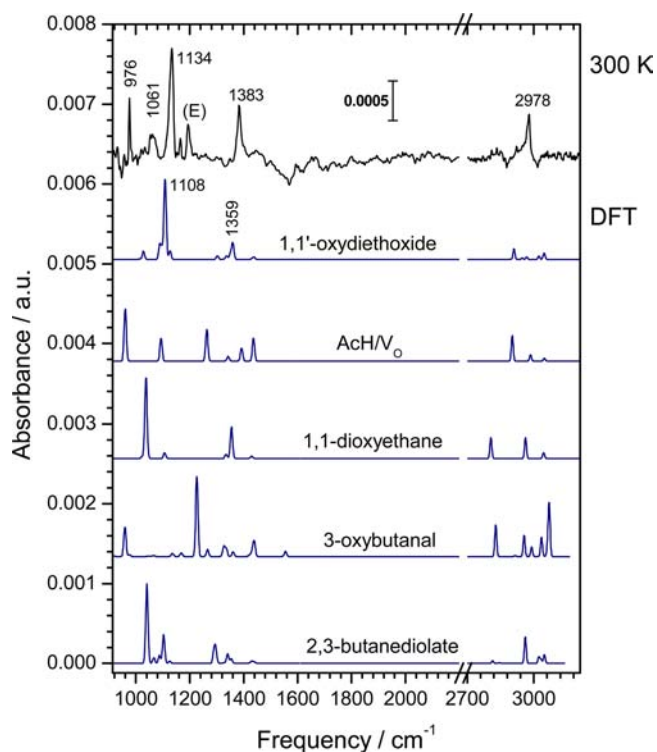


Figure 3. RAIRS spectrum obtained for acetaldehyde adsorbed on highly reduced $\text{CeO}_{2-x}(111)$ at 175 K followed by annealing to 300 K (top curve). For comparison, the DFT-calculated spectra for several oxygen vacancy-stabilized AcH states (see Figure 2c–g) are shown.

peak at 1194 cm^{-1} (labeled E) is attributed to a minority enolate state (discussed below).

Given that two waves of molecular AcH desorption occur at 400 and 550–600 K,³⁴ evidently a major portion of the AcH molecules remain on the surface past 220 K and are transformed, reversibly, into an alternate form, promoted by the reduced surface. To explain the experimentally observed spectrum obtained after annealing to 300 K, we considered several possible AcH states stabilized by an oxygen vacancy. The DFT-optimized structures for these states are shown in Figure 2. The simplest possibility is an AcH molecule adsorbed in an oxygen vacancy (denoted AcH/ V_o ; Figure 2c). The acyl C of the AcH/ V_o could form an additional bond with an adjacent

lattice O. This structure can be viewed as a dioxy (formally 1,1-dioxyethane) partially occupying two adjacent oxygen vacancies (Figure 2d) because the two oxygen atoms are chemically equivalent and because the distance between adjacent oxygen sites is too far for the molecule to completely occupy both sites simultaneously. DFT predicts a strong peak at 1040 cm^{-1} for this dioxy state that does not agree with the dominant 1134 cm^{-1} peak observed (Figure 3), and it is slightly less stable than AcH/ V_o (Table 2).

We also considered three possible coupling products between two AcH molecules that are stabilized by oxygen vacancies. First is from C–O bond coupling between the carbonyl O of an AcH and the acyl C of an AcH/ V_o . The minimum-energy structure for the C–O dimerized state (formally 1,1'-oxydiethoxide occupying two adjacent oxygen vacancies) is shown in Figure 2e. This type of C–O bond coupling to form polymers has been reported previously on several metal surfaces^{66,69,73–75} and on some oxide surfaces for AcH^{58,76,77} and acetone.⁶⁷ C–C bond coupling forming C_4 species was also considered, either between the acyl C's of an AcH and an AcH/ V_o to form 2,3-butanediolate (Figure 2f) or between the acyl C of an AcH and the α -C of the enolate to form 3-oxybutanal (Figure 2g). Coupling between acyl C in AcH has been proposed theoretically⁷⁸ as the intermediate in the reaction pathway for production of 2-butene from acetaldehyde adsorbed on $\text{TiO}_2(110)$ in UHV.⁷⁹

The calculated vibrational spectra for the five vacancy-stabilized AcH states are shown in Figure 3 with the experimental data, and their adsorption energies are listed in Table 2. All five are more stable than the η^1 -O AcH on $\text{CeO}_2(111)$. This is consistent with previous reports of vacancy stabilization for alkoxy and carboxylate groups.^{35,80} The AcH/ V_o , dioxy, and 3-oxybutanal states are similar in energy, whereas 1,1'-oxydiethoxide and 2,3-butanediolate are $\sim 0.2\text{ eV}$ more stable per AcH unit. None of these states exhibit a vibrational peak near 1700 cm^{-1} that is indicative of a carbonyl bond, consistent with the experimental spectrum. Various peaks are found around 2900 cm^{-1} due to the methyl groups in all five states.

A comparison of the spectra in Figure 3 suggests that the calculated IR spectrum of 1,1'-oxydiethoxide (the C–O dimerized state) corresponds most closely to the experimentally observed spectrum for $\text{CeO}_{2-x}(111)$ after annealing to 300 K. It is also the most stable among the intermediates considered

Table 3. Experimental and Calculated Values of IR-Active Vibrations (in cm^{-1}) Assigned to 1,1'-Oxydiethoxide Obtained from Adsorption of Acetaldehyde- h_4 on Reduced $\text{CeO}_{2-x}(111)$ at 175 K and Annealing to 300 K^a

	present work	present work (DFT)	AcH/ WO_3 , ref 58	AcH+O/Ag, ref 74	poly-AcH, ref 81
$\nu_a(\text{CH}_3)$		3047, 3023	2988	2975, 2960	
$\nu_s(\text{CH}_3)$	2978	2948–2968	2938		
$\nu(\text{CH})$		2911		2838	
$\delta_a(\text{CH}_3)$		1438	1447	1442	
$\delta_s(\text{CH}_3)$	1383	1359	1382	1376	1379
$\delta(\text{CH})$		1337, 1303	1345	1326	1340
$\nu_a(\text{OCO})$	1166	1127	1199	1175	
			1146	1160	
$\nu_s(\text{OCO})$	1134	1108	1099	1090	
		1090	1043	1084	
$\nu(\text{CC}) + \nu(\text{C–O})$	1061 (broad)	1028		1122	1041 (br)
$\rho(\text{CH}_3)$	976 ^b		970	915, 904	

^aAll references cited in the table are for acetaldehyde or acetone polymers for comparison. ^bPossible artifact.

(Table 2). It contains two main IR-active modes at 1359 and 1108 cm^{-1} , which correspond well to the observed peaks at 1383 and 1134 cm^{-1} . The calculations indicate that the 1383 cm^{-1} peak is due to methyl deformation, $\delta(\text{CH}_3)$, and the 1134 cm^{-1} peak is due to $\nu_s(\text{O}-\text{C}-\text{O})$, although this mode is considerably coupled to C–C stretching. No C=O stretch is detected because neither of the two types of C–O bond in the dimerized state is a carbonyl. The original carbonyl bond has elongated to ~ 1.40 Å, approaching that of an alcohol C–OH single bond (cf. gas-phase ethanol, Table 2), and the C–O–C bond is even longer than a typical ether C–O–C bond at ~ 1.47 Å (cf. gas-phase diethyl ether, Table 2). The assignments of the vibrational features for the C–O dimerized state are summarized in Table 3 together with literature reported values for polymeric AcH. The polymerization of aldehydes and ketones proceeding through the carbonyl O of one molecule attacking the activated acyl C of a second molecule is known to result in linear polyacetals with $(-\text{R})\text{C}-\text{O}-\text{C}(\text{R})-$ bonds. A recent study of AcH adsorption on thin WO_3 films has presented RAIRS spectra very similar to the one presented in Figure 3.⁵⁸ In particular these authors assigned a region from 1100 to 1200 cm^{-1} with somewhat broad features to the $\nu(\text{O}-\text{C}-\text{O})$ vibrations of AcH polymers. Our results also compare well with the vibrational features of poly-AcH on $\text{Ag}(111)$ ⁷⁴ and bulk poly acetaldehyde^{76,81} (given in Table 3). Henderson concluded that acetone adsorption on TiO_2 results similarly in the formation of poly acetone based on HREELS.⁶⁷ The existence of C–O higher multimers cannot be completely ruled out in our experiments, although the sharp peaks observed in the IR spectrum (Figure 3) suggest that the surface species is structurally uniform, and substantial polymerization is probably limited by the coverages of oxygen vacancies in the present experiments. Further support of the IR assignments is presented in the Supporting Information section where experimental data for experiments with perdeuterated AcH (AcH- d_4) is presented together with the calculated IR spectrum for the d_4 C–O dimerized state (see Supplementary Figure S2 and Table S3).

When the C–O dimerized state is further annealed to 400 K, new features were observed in the RAIRS (Figure 4) that are different both from the $\eta^1\text{-O}$ AcH and from the C–O dimerized state. This change signals the appearance of yet another state, which we assign to the enolate that is stabilized by an oxygen vacancy, as described below. In the RAIRS there is strong absorption at 1600 cm^{-1} that is indicative of a C=C stretch, which can form after the dehydrogenation of the methyl group; and a small peak at 3650 cm^{-1} that corresponds to O–H stretch from hydroxyls formed on the ceria surface further corroborating the dehydrogenation step. The peaks at 1404 and 1317 cm^{-1} are due to HC= and =CH₂ deformations. A vibration at 1194 cm^{-1} was already observed in the 300 K spectrum (Figure 3; peak labeled E) and is assigned to the C–O stretch of this enolate interacting with the surface through an oxygen vacancy. This C–O stretching frequency is considerably blue-shifted compared to the values for adsorbed alkoxys, found at 1060 cm^{-1} for ethoxy⁷⁰ on CeO_2 or at 1040 cm^{-1} typically found for methoxide, indicative of increased bond order. Finally, a set of vibrations are seen in the region 977–960 cm^{-1} that could correspond to CH=CH₂ twisting/rocking. Vinylic C–H stretches should be seen in the 3000–3200 cm^{-1} region but are not visible in the present experiments. The vibrational assignments for the enolate are summarized in Table 4, together with available reference data of

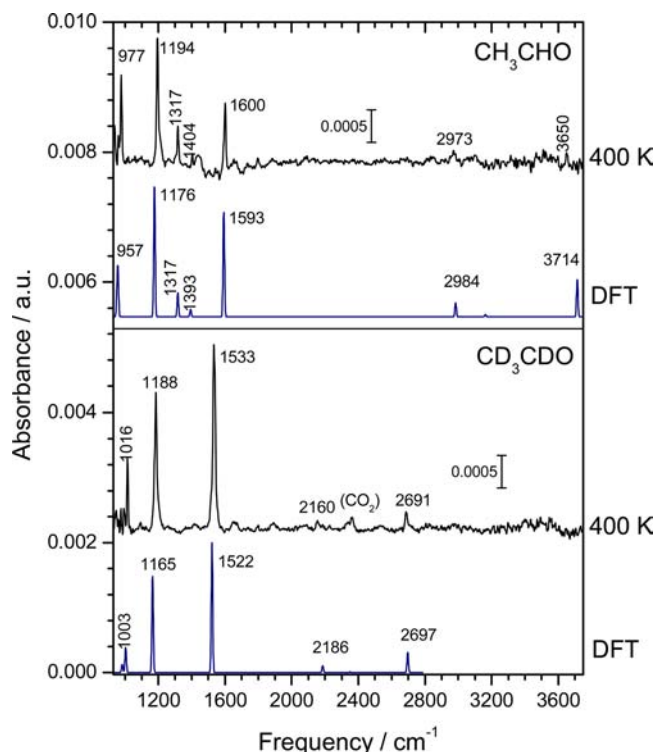


Figure 4. RAIRS spectra obtained for adsorption of acetaldehyde (upper panel) and perdeuterated acetaldehyde (lower panel) at 175 K on highly reduced $\text{CeO}_{2-x}(111)$ followed by annealing to 400 K. For comparison, the DFT-calculated IR spectra for the enolate and perdeuterated enolate states are shown.

vinyl alcohol⁸² and enolate from AcH on Co and Ag supported on Al_2O_3 .^{32,33} Enolate formed by acetone adsorbed on other oxides have also been reported and a C=C bond has been identified near 1550–1650 cm^{-1} .^{30,83,84}

Transformation of the C–O dimerized state present at 300 K to the enolate at 400 K is also supported by DFT, and the calculated minimum-energy structure for enolate is shown in Figure 2h. The carbonyl oxygen of the enolate is stabilized by an oxygen vacancy, with the dissociated H co-adsorbed on an adjacent lattice O forming a surface hydroxyl group, consistent with the general view that on ceria the basicity is related to surface O^{2-} species and acidity to surface Ce cations.⁸⁵ This state (denoted enolate/ $\text{V}_\text{o}+\text{H}$) is more stable than the C–O dimerized state by 0.62 eV (Table 2). The calculated C–C bond length has contracted to 1.350 Å, comparable to 1.331 Å in gas-phase ethylene and 1.332 Å in gas-phase vinyl alcohol (Table 2), which is clearly a C=C double bond in nature. The calculated C–O bond length is 1.350 Å, intermediate between a saturated alcohol (cf. 1.433 Å in gas-phase ethanol, Table 2) and a carbonyl (cf. 1.219 Å in gas-phase AcH, see Table 2), consistent with the observed C–O stretch that is blue-shifted compared to single C–O bonds. For comparison the calculated C–O bond length for the enol form of acetone is 1.37 Å.^{30,86} The calculated IR spectrum of enolate/ $\text{V}_\text{o}+\text{H}$ agrees very well with experiment (Figure 4). The calculated intensities for the $\nu(\text{CH}_2)$ vinylic stretch are weak, which explains why they are not observed experimentally.

To further corroborate these assignments, the same experiment was performed using AcH- d_4 , and the experimental results are shown in Figure 4 (lower panel) together with the DFT-calculated spectrum for the case of perdeuterated enolate/

Table 4. Experimental and Calculated Values of IR-Active Peaks Assigned to the Enolate Obtained from Adsorption of Acetaldehyde- h_4 and d_4 on Reduced CeO_{2-x} (111) and Annealing to 400 K^a

assignment	present work	present work (DFT)	vinyl alcohol		AcH	
			ref 98	ref 82	ref 33	ref 32
$\nu(\text{OH})$ (surf)	3650 (2691)	3714 (2697)	3625 (2677)	3619 (2672)		
$\nu_a(\text{CH}_2)$	n/o	3162 (2350)	3242 (2411)			
$\nu_s(\text{CH}_2)$	n/o	3064 (2239)				
$\nu(\text{CH})$	2973 (2160)	2984 (2186)				
$\nu(\text{C}=\text{C})$	1600 (1533)	1593 (1522)	1631, 1625 (1590, 1584)	1648 (1583)	1633 ^b	1612 ^b
δCH_2	1404 (1016)	1393 (1003)			1416 ^c	1424 ^c
δCH	1317 (992)	1317 (983)			1336	1350
$\nu(\text{C}-\text{O})$	1194 (1188)	1176 (1165)	1079, 1084 (923, 926)	1090		
$\rho(\text{CH}=\text{CH})$ twist	977	957				

^aThe frequency values in parentheses corresponds to $\text{CD}_2=\text{CDO}-\text{Ce} + \text{D}$ species. n/o = not observed. ^bAssigned by authors to $\nu_s(\text{C}=\text{C}-\text{O})$
^cAssigned by authors to $\nu_a(\text{C}=\text{C}-\text{O})$.

V_o co-adsorbed with d -hydroxyl. Again the agreement between experiment and theory is excellent, and the correct shifts due to deuteration are captured by the calculations. The OD stretch is seen at 2691 cm^{-1} and calculated at 2697 cm^{-1} . Experimentally the C=C and C-O stretches are seen at 1533 and 1188 cm^{-1} respectively, while the corresponding calculated frequencies are at 1522 and 1165 cm^{-1} . The DFT calculations and experiment agree in both the direction and the magnitude of the isotopic shifts. Deuteration causes the C=C stretch to red-shift by 67 cm^{-1} (71 cm^{-1} calculated), while the C-O stretch is red-shifted by 6 cm^{-1} (11 cm^{-1} calculated). Our observed C=C redshift matches that observed for gas-phase vinyl alcohol (65 cm^{-1}).⁸² A smaller redshift for the C-O stretch is due to weak coupling of this mode to the other modes of the molecule. The vibrational assignments for the perdeuterated enolate are also summarized in Table 4.

3.3. DFT-Calculated Reaction Pathways for Acetaldehyde. To further corroborate the identities of the proposed surface intermediates based on the experimentally observed and DFT-calculated IR spectra, we performed additional DFT calculations to determine the activation barriers along the reaction pathways consisting of the proposed surface intermediates and performed kinetic analysis based on the activation barriers to verify whether the reaction pathways are consistent with our previous TPD observations.

On $\text{CeO}_2(111)$, AcH desorbs molecularly without further reaction at 210 K.³⁴ We assumed the desorption of the $\eta^1\text{-O}$ AcH to be a first-order process. The classic Redhead analysis⁸⁷ was applied:

$$-r = \frac{d\theta_{A^*}}{dt} = \nu e^{-E_a/kT} \theta_{A^*}$$

where r is the rate of disappearance (or desorption) of the species A (here AcH); θ_{A^*} is the surface coverage of A; ν is the pre-exponential factor; E_a is the activation barrier for the desorption process; k is the Boltzmann constant; $T = T_0 + \beta \cdot t$ where T_0 is the initial temperature and β is the heating rate (set to 2 K/s as in our previous TPD study³⁴). The peak desorption temperature is then defined by $(dr/dT) = 0$. For a lack of precise knowledge of the nature of the TS for the desorption process, ν is set to a typical value of 10^{13} s^{-1} , and E_a is set to the negative of the adsorption energy of the $\eta^1\text{-O}$ AcH state, and here the $1/4 \text{ ML}$ coverage value of -0.20 eV is used. This led to the prediction that the peak desorption temperature should be 77 K , considerably lower than the observed desorption peak at 210 K in TPD. Given the weak chemical interaction between

AcH and $\text{CeO}_2(111)$, we recalculated the $\eta^1\text{-O}$ state using the optB86b van der Waals density functional.^{88,89} The vdW-corrected bulk lattice constant for CeO_2 was 5.452 \AA at $U = 2 \text{ eV}$, and the adsorption energy for AcH was -0.43 eV at $1/4 \text{ ML}$. This value brought the predicted peak desorption temperature to 162 K , in closer agreement with the TPD results.

The interpretation of the RAIRS spectra together with the DFT calculations suggests a different reaction pathway for AcH on $\text{CeO}_{2-x}(111)$ from that on $\text{CeO}_2(111)$. The calculated reaction energy profile for AcH on $\text{CeO}_{2-x}(111)$ is shown in Figure 5. The entire pathway is constrained to having a magnetic moment of 2 because it is either the lowest-energy state or is within 0.05 eV of the lowest energy state for every local minimum and TS along the pathway. Note that since TPD is not an equilibrated procedure, the reaction energy

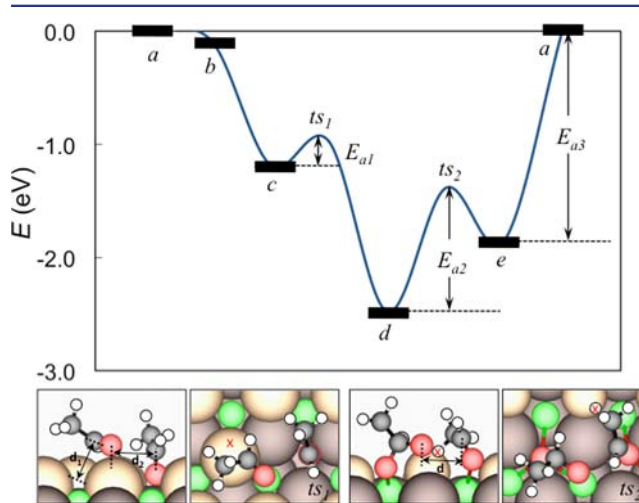


Figure 5. Energy profile for the proposed main reaction pathway for AcH on $\text{CeO}_{2-x}(111)$. E is the ZPE-corrected DFT total energy (in eV). The states along the pathway are (a) two gas-phase AcH with a surface oxygen vacancy; (b) one AcH in $\eta^1\text{-O}$ state; (c) second AcH in V_o ; (d) C-O dimerized state; (e) enolate/ V_o +H plus one AcH back in gas phase. The structures for ts_1 and ts_2 are shown in top and side views below the plot; “X” marks the bonding lattice O atom in ts_1 and the dissociating H in ts_2 . The labeled bond distances are referred to in the text. The forward E_a are $E_{a1} = 0.19 \text{ eV}$, $E_{a2} = 1.09 \text{ eV}$, and $E_{a3} = 1.86 \text{ eV}$. $\eta^1\text{-O}$ AcH (in b and c) is calculated at $1/2 \text{ ML}$; all other adsorbates at $1/4 \text{ ML}$. In a, b, c, and e, E is calculated for the two AcH molecules in separate unit cells.

Table 5. DFT-Calculated Key Adsorption Energy (ΔE in eV; Relative to Gas-Phase AcH); Activation Barrier (E_a in eV) and Corresponding Peak Reaction Temperature (T_p in K); Oxygen Vacancy Formation Energy (ΔE_v in eV); and Key Vibrational Frequencies (in cm^{-1}) Computed at $U = 0, 2$ and 5 eV^a

	ΔE			E_a (and T_p) ^b			key frequency ^c		
	$U = 0$	$U = 2$	$U = 5$	$U = 0$	$U = 2$	$U = 5$	$U = 0$	$U = 2$	$U = 5$
H (isolated -OH)	-2.71	-2.72	-3.18				3734	3745	3739
AcH (η^1 -O)	-0.19	-0.20	-0.23						
AcH (η^1 -O, 1/2 ML)	-0.09	-0.09	-0.11				1714	1712	1711
AcH (μ -C,O)	-0.53	-0.53	-0.55				1002	1002	1014
AcH/ V_o	-1.13	-1.09	-1.11						
1,1'-oxydiethoxide (C–O dimerized)	-1.18	-1.24	-1.41	+1.15 (390)	+1.09 (360)	+1.39 (523)	1106	1108	1109
enolate/ V_o ^d	-1.76	-1.86	-2.24	+1.76 (527)	+1.86 (556)	+2.24 (666)	1586	1593	1590
							1177	1176	1182
ΔE_v , surface point oxygen vacancy	+3.52	+3.49	+2.76						

^aAll energies are corrected by zero-point energies. Results are calculated at 1/4 ML coverage except where noted. ΔE for C–O dimer is averaged over two AcH. ^b E_a and T_p are for 1,1'-oxydiethoxide decomposition to enolate/ V_o and for enolate/ V_o desorption as AcH. A prefactor of 10^{16} s^{-1} is assumed for enolate desorption. ^cKey vibrational frequencies correspond to the calculated mode(s) with the highest intensity in Figures 1, 3, and 4. ^dDenotes that the state includes a dissociated hydrogen in the form of a co-adsorbed surface hydroxyl.

profile is only operative in the forward direction. Reaction begins with an AcH adsorbed on the oxidized part of the surface (represented by the η^1 -O state) and an AcH adsorbed in an oxygen vacancy as AcH/ V_o . The transition state of the coupling step involves two nascent C–O bonds, one between the acyl C of the attacking AcH and a lattice O at $d_1 = 2.537 \text{ \AA}$, the other between the carbonyl O of the attacking AcH and the acyl C of the AcH/ V_o at $d_2 = 2.619 \text{ \AA}$ (ts_1 , Figure 5). This step converts an equal number of AcH and AcH/ V_o into the C–O dimerized state (Figure 2d). To simplify the analysis, we assume that the coupling step, which involves a loosely bound AcH and an AcH/ V_o that is immobile at low temperature, to be first-order in the coverage of AcH/ V_o , and apply the same Redhead analysis described earlier. The calculated E_a is 0.19 eV (Figure 5), and ν is $3.8 \times 10^{11} \text{ s}^{-1}$ based on the harmonic approximation as $(\prod_i \nu_i^{\text{IS}} / \prod_j \nu_j^{\text{TS}})$.⁴⁶ A peak reaction temperature of 82 K for the formation of the dimerized state is predicted, consistent with the detection of the dimerized state in RAIRS at as low as 110 K (data not shown).

Conceivably some AcH molecules fail to dimerize depending on the surface concentration of oxygen vacancies. Isolated AcH/ V_o can decompose to enolate via the transfer of an α -H (from the methyl end) to a lattice O. Redhead analysis based on the calculated E_a of 0.27 eV and ν of $1.3 \times 10^{12} \text{ s}^{-1}$ (not shown in Figure 5) suggests a peak reaction temperature of 110 K for the formation of the enolate/ V_o +H from AcH/ V_o . Thus near and below 220 K the enolate could form on the CeO_{2-x} (111) surface. The RAIRS results were consistent with a small amount of enolate coexisting with the C–O dimerized state at 200 K (data not shown) and 300 K (peak E , Figure 3).

C–O coupling functions as a surface reservoir of AcH that is responsible for the desorption of AcH at higher temperature than on fully oxidized CeO_2 (111).³⁴ The C–O dimer could decompose back into AcH and AcH/ V_o but can also decompose via the breaking of C–O–C linkage and the concerted loss of a α -H, into AcH, enolate/ V_o , and a surface hydroxyl, with a lower activation barrier (ts_2 , Figure 5). In the transition state ts_2 the dissociating C–O bond is at $d = 2.603 \text{ \AA}$. The AcH is no longer stable on the surface at the elevated temperature and therefore immediately desorbs. Redhead analysis based on calculated E_a of 1.09 eV (Figure 5) and ν of $3.6 \times 10^{14} \text{ s}^{-1}$ suggests a peak reaction temperature of 360 K for the decomposition of the dimerized state, somewhat lower

than the observed second wave of AcH desorption at 400 K. This interpretation that the desorption at 400 K derives from decomposition of the dimer differs from the previous explanation, which attributes the desorption peak at 400 K to AcH stabilized at a vacancy.³⁴

The previous TPD results indicate that the recombinative desorption of enolate and H as AcH competes with the decomposition of the enolate that oxidizes the surface and produces gaseous C_2 hydrocarbon products as well as H_2 .³⁴ The high-temperature decomposition pathways are not the main focus of this study and are not considered in our calculations, but what can be concluded is that there is an appreciable amount of H on the surface from the decomposition of some of the enolate. Therefore, we assume the recombinative desorption of enolate with mobile and plentiful H to be first-order. Redhead analysis based on the adsorption energy of the enolate/ V_o +H state of -1.86 eV (Figure 5) and a high pre-exponential factor of 10^{16} s^{-1} for high-temperature desorption processes⁹⁰ suggests a peak temperature of 556 K, in agreement with the observed third wave of AcH desorption 550–600 K.

Finally, we compare several key energetic and vibrational quantities calculated using different values of U , including $U = 0, 2,$ and 5 eV (Table 5). A salient feature, consistent with our previous findings for formic acid adsorption on CeO_2 (111) surfaces,³⁵ is that vibrational frequencies are insensitive to the value of U beyond what may be attributed to the small change in the lattice constant. The same is not always true for surface energetics. While the adsorption energies of molecular AcH vary by less than 0.05 eV from $U = 0$ to 5 eV, those of open-shell species, i.e., the C–O dimer and the enolate plus H, vary noticeably with U . Our results suggest that the effect of U on adsorption energy is stronger for systems with less stabilized unpaired electrons, particularly those involving a surface H atom or oxygen vacancy, in keeping with our previous findings.³⁵ This is because such electrons are transferred to Ce^{4+} cations, and a higher U value encourages electron localization by making the localized state more stable than delocalized states. These results provide one of the first reports that the activation barrier of a surface reaction involving such a species is also affected by U . The predicted peak reaction temperatures for $U = 5 \text{ eV}$ clearly exceed the observed AcH desorption waves at 400 and 550–600 K. Previously a low U of

2–3 eV was suggested to yield better reduction energies for bulk ceria,^{50,51} and Huang and Fabris reported that $U = 2\text{--}3$ eV produced better agreement between calculated and measured CO adsorption energies on $\text{CeO}_2(110)$.⁹¹ The present results contribute additional evidence for the performance of different U values for surface chemistry on ceria based on comparing experimentally measured and calculated energetic and vibrational quantities.

4. DISCUSSION

Previous TPD, sXPS, and NEXAFS results³⁴ and current RAIRS and DFT results have revealed richer chemistry for AcH on the reduced compared to the fully oxidized $\text{CeO}_2(111)$ surface. The two higher-temperature desorption states and surface intermediates found on the reduced surface not only indicate a stronger interaction with the surface but also signal that two types of states or competing processes are occurring. It is well-known that aldehydes (and carbonyl compounds in general) can act both as nucleophiles and as electrophiles under appropriate conditions.⁹² In aldol addition, for instance, an aldehyde with an α -H is converted to its enolate form that acts as the nucleophile to attack the electrophilic acyl C of another aldehyde. The enolization of an aldehyde requires base-catalyzed α -H abstraction, and the acceptor aldehyde requires stabilization of the carbonyl O by an acid. The lack of reaction for AcH on the fully oxidized $\text{CeO}_2(111)$ surface suggests that although lattice Ce^{4+} cations are acidic, they are evidently unable to stabilize the carbonyl O. The η^1 -O AcH remains mostly vdW bonded to the surface, and the carbonyl O is 2.689 Å from the Ce, larger than bulk-like Ce^{4+} -O bonds (Table 2). Also the lattice O^{2-} anions are not basic enough to activate an α -H abstraction, even though the α -H in AcH is relatively acidic.^{4,5}

However, introducing an oxygen vacancy in the surface opens a 3-fold hollow site where Ce cations are more accessible, redistributes surface charge, and introduces Ce^{3+} cations. It is likely that a combination of these factors enables the activation of the carbonyl bond of an AcH that migrates into this site and opens it for coupling reactions, despite the fact that the acyl C of this AcH/ V_o is less positively charged than in the η^1 -O state (see Bader charges in Table 2). DFT calculations indicate that an oxygen vacancy and a lattice O^{2-} anion, combined, enable enolate formation, exemplifying the bifunctional nature of this surface; namely, AcH/ V_o can undergo α -H abstraction by a lattice O^{2-} anion to form the enolate (enolization) with a small barrier (0.27 eV). However, because the carbonyl of the AcH/ V_o is already stabilized and activated by the vacancy, carbonyl self-reaction is observed instead, i.e., the carbonyl O of another AcH acts as the nucleophile to attack the acyl C of the AcH/ V_o , leading to the C–O dimerized state (Figure 2e). This self-reaction is competitive with enolization at low temperatures because the activation barrier is lower (0.19 eV).

Two incidental points are to be made regarding C–O coupling reactions for AcH. First, surface O or hydroxyl groups on metal surfaces are known to perform nucleophilic attack on AcH at the acyl C position.^{93,94} Reactive attack by surface oxygen has been observed previously as in the reaction of AcH with co-adsorbed oxygen (either as $\text{O}_{2,a}$ or O_a) to form an AcH-oxygen complex on TiO_2 ⁷⁹ and is predicted when a lattice oxygen attacks to form a “doubly bonded CH_3CHO configuration” on reduced MoO_3 .⁹⁵ The formation of such a dioxy species has also been proposed for formaldehyde

adsorption on reduced $\text{CeO}_2(111)$ ⁷¹ and on anatase TiO_2 .⁹⁶ Moreover, the formation of a dioxy is typically followed by disproportionation. We do not observe the corresponding formation of ethoxy and acetate at 300 K or higher on the reduced CeO_2 . Second, polymerization via the carbonyl O of one AcH molecule attacking the acyl C of a second AcH molecule is generally known to occur. Furukawa et al.⁸¹ have studied the polymerization of AcH on different oxide surfaces and found that only Al_2O_3 was very active for catalyzing this reaction. They proposed that C–O–C bond formation goes through a cationic mechanism and that Al cations play an important role in initiating the polymerization reactions. As mentioned above, however, polymerization beyond the dimer formation is concluded not to be the major pathway in our experiments.

The C–O dimerized state is not a closed-shell species and cannot escape into gas phase as a molecule. It dissociates at 400 K to form the enolate. The presence of the enolate at 400 K and above is concluded from the RAIRS spectrum, and the excellent agreement with the DFT-calculated IR spectra for the enolate and perdeuterated enolate provides further support for this conclusion. Previously Chen and Mullins³⁴ concluded from XPS and NEXAFS that the adsorption of AcH under the same experimental conditions as used here resulted in a carbanion state formed by the cleavage of a methyl C–H bond ($[\text{O}-\text{CH}-\text{CH}_2]^-$) to form a hemicycle, in which both the α -C and carbonyl O atoms are bonded to Ce cations. Ambiguity resulted from the inability to determine which part of the molecule has the localized charge and from the possession of both C=O and C=C character by the molecule as seen in NEXAFS. However, DFT calculations indicate that it does not form such a hemicyclic structure, and instead suggest a complete C=C bond (corresponding to the 1600 cm^{-1} peak in Figure 4) and a rehybridized C–O single bond (corresponding to the 1194 cm^{-1} in peak Figure 4). Recent work by Chen and Mullins⁹⁷ on ethylene glycol adsorption on ceria has reinterpreted similar features in the NEXAFS spectra as due only to C=C bonds.

The availability of the enolate may lead one to expect aldol addition products. Indeed, the formation of crotonaldehyde has been reported on ceria powder.²⁵ Yet there is no evidence in the TPD³⁴ or RAIRS of crotonaldehyde, the α - β unsaturated condensation product formed by two AcH molecules, its precursors (3-oxybutanal), or any other C_4 product. We attribute the lack of aldol addition to the fact that the decomposition of the dimer leaves only enolate and H on the surface. Because no AcH remains on the surface above 400 K except as enolate, C–C bond coupling toward crotonaldehyde formation is prevented even though there is enolate. The nature of our present experiments therefore imposes a coverage limitation that is not conducive to aldol additions; molecular AcH is available on the surface at low temperatures but not at high temperatures. Previous work has shown that aldol condensation does occur on CeO_2 powder and on TiO_2 single crystal surfaces.^{22,25} We also speculate that different crystalline facets of CeO_2 may more effectively activate the carbonyl, perhaps without an oxygen vacancy. Experiments are in progress to demonstrate how aldol addition can be induced on ceria surfaces by taking these findings into consideration.

5. CONCLUSIONS

Comparison of TPD, RAIRS, and DFT+U calculations have provided a comprehensive picture of how acetaldehyde (AcH) reacts on $\text{CeO}_2(111)$. AcH predominantly adsorbs weakly in

η^1 -O configuration on the fully oxidized CeO₂(111) surface without reaction. On the reduced CeO_{2-x}(111) surface, the oxygen vacancy plays the key role of stabilizing the carbonyl group, thereby opening AcH both to nucleophilic attack at the acyl C, and to enolization. Calculated rate parameters predict that both the nucleophilic C–O coupling and the enolate formation are facile at low temperatures, with the former being more so than the latter. The low temperature conditions in our experiments favor C–O coupling over enolate formation, leading to the retention of AcH above 210 K, the temperature at which AcH on the fully oxidized surface desorbs. The C–O coupled dimer dissociates into enolate, H, and a desorbing AcH at 400 K. Although enolates from acetone have been observed on metals and hypothesized on various oxides, to our knowledge this is the first conclusive identification of the enolate form of AcH on ceria. The enolate is stable on the surface to about 550 K, where its desorption is observed in part through recombination as AcH. Aldol addition is not observed despite the formation of the enolate because of the competing nucleophilic addition reaction at low temperatures and because of the limited coverage of AcH at elevated temperatures in the UHV condition of our experiments. These factors will need to be taken into consideration if CeO₂(111) or ceria in general is to be adapted as an aldol condensation catalyst. Our DFT results provide additional evidence that calculated vibrational frequencies are insensitive to the value of the *U* parameter, but a large *U* value can lead to predictions that diverge from experiments (TPD measurements) for reactions involving vacancy-bound open-shell species on oxide surfaces.

■ ASSOCIATED CONTENT

📄 Supporting Information

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Notes

The authors declare no competing financial interest.

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