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Adsorption and Reaction of C<sub>1</sub>–C<sub>3</sub> Alcohols over CeO<sub>x</sub>(111) Thin Films<sup>†</sup>D. R. Mullins,\* S. D. Senanayake,<sup>‡</sup> and T.-L. Chen

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This study reports the interaction of methanol, ethanol, 1-propanol, and 2-propanol with well-ordered CeO<sub>2</sub>(111) thin film surfaces. All of the alcohols adsorb at low temperature by forming alkoxy and hydroxyl species on the surface. On fully oxidized CeO<sub>2</sub>(111), recombination occurs between some of the alkoxy and hydroxyls, resulting in alcohol desorption near 220 K. At the same temperature, some of the surface hydroxyls disproportionate to produce water and the loss of lattice O. The remaining alkoxy species react above 550 K. The primary alcohols favor dehydrogenation products (aldehydes). There is a net loss of O from the system, resulting in a reduction of the ceria. The secondary alcohol, 2-propanol, undergoes primarily dehydration, producing propene with no net change in the cerium oxidation state. Reduced CeO<sub>x</sub>(111) competes with the gaseous products for available O. Little or no water is produced. The reaction selectivity for the C<sub>2</sub> and C<sub>3</sub> alcohols shifts toward favoring dehydration products. The loss of O from the alcohols leads to oxidation of the reduced ceria. Compared with the oxidized surface, the alkene desorption shifts to lower temperature, whereas the aldehyde desorption shifts to higher temperature. This indicates that, on the reduced surface, it is easier to break the C–O bond but more difficult to break the O–substrate bond.

## 1. Introduction

Alcohol adsorption and reaction is a classic probe for characterizing the catalytic properties of oxide materials.<sup>1,2</sup> The adsorption of alcohols can be used to determine the number of active sites on the surface. In this regard, the simplest alcohol, methanol, can provide the most straightforward answer. The reactions of more complicated alcohols, such as ethanol and propanol, can be used to characterize the acidic or basic nature of the oxide. The standard interpretation is that these alcohols will undergo dehydration with acidic oxides to produce alkenes and water. Alcohols undergo dehydrogenation on basic oxides to form aldehydes (or ketones) and hydrogen.

This characterization is an oversimplification however. Alcohol reactions on oxides can often produce a mixture of dehydration and dehydrogenation products.<sup>3–5</sup> It has also been demonstrated that reactions on well-characterized, single-crystal surfaces can differ from results obtained from more heterogeneous, powder surfaces.<sup>3–8</sup> This suggests that the structure of a given oxide, and not just its composition, may be critical in establishing its reactivity.

The very terms “dehydration” and “dehydrogenation” may also be misleading. They correctly describe what is removed from the reactant alcohol when a certain C-containing product is produced. However, they do not encompass the possible involvement of oxygen atoms, or oxygen vacancies, in the substrate. A dehydrogenation reaction may produce water as a product if the H that leaves the alcohols reacts with O in the substrate to produce water. Conversely, a dehydration reaction may produce H<sub>2</sub> as a product if the O from the alcohol fills an O vacancy in the substrate. We have previously observed this type of behavior in the reactions of simple C<sub>1</sub> oxygenates on CeO<sub>2</sub>(111) thin films. Methanol undergoes dehydrogenation to

produce formaldehyde or CO, but it also reacts with O from the ceria to produce water.<sup>9</sup> Formic acid dehydrates to produce CO on reduced CeO<sub>x</sub>(111), but the oxygen removed from the reactant fills O vacancies in the reduced ceria.<sup>10</sup>

Previous studies have characterized the behavior of C<sub>1</sub> oxygenates on CeO<sub>x</sub>(111) thin films.<sup>9–11</sup> These reactants provide a somewhat limited picture, however, because they lack extended hydrocarbon chains. The C<sub>1</sub> oxygenates generally do not produce products that exhibit C–O bond cleavage. The exception is formic acid where one of the C–O bonds is broken to produce CO.<sup>10</sup> C<sub>2</sub> and C<sub>3</sub> alcohols provide an additional reaction pathway where unsaturated alkene products can result from C–O bond cleavage.

In this study, we have observed that all of the alcohols are highly reactive on both oxidized and reduced CeO<sub>x</sub>(111) thin films. The primary alcohols tend to favor dehydrogenation products (aldehydes), whereas the secondary alcohol exhibits dehydration almost exclusively. Reduction of the ceria, which results in O vacancies on the ceria surface, promotes dehydration of the alcohols as the substrate competes with the products for the available O.

## 2. Experimental Section

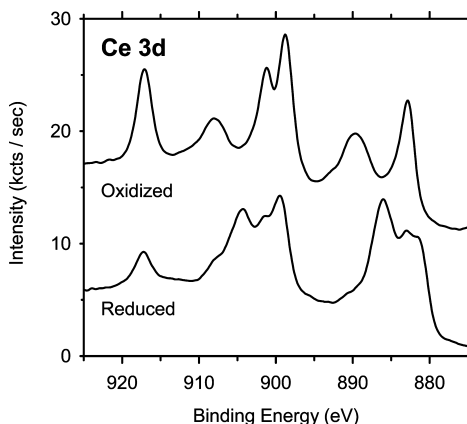
Experiments were performed in two separate UHV chambers. Soft X-ray photoelectron spectroscopy (sXPS) was conducted using synchrotron radiation on beamline U12a at the National Synchrotron Light Source (NSLS). Ce 3d XPS and temperature-programmed desorption (TPD) was performed in a separate chamber at Oak Ridge National Laboratory (ORNL).

C 1s spectra were recorded using a photon energy of 400 eV. 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.<sup>9,12</sup> The U12a beamline was recently modified with the addition of a Ni-coated refocusing mirror at the final stage before the sample. This mirror focuses the X-ray into a spot ca. 1 mm × 1 mm that is well matched to the electrostatic analyzer's 1 mm<sup>2</sup> analysis area. This modifica-

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**Figure 1.** Ce 3d XPS spectra from oxidized CeO<sub>2</sub>(111) and reduced CeO<sub>1.67</sub>(111).

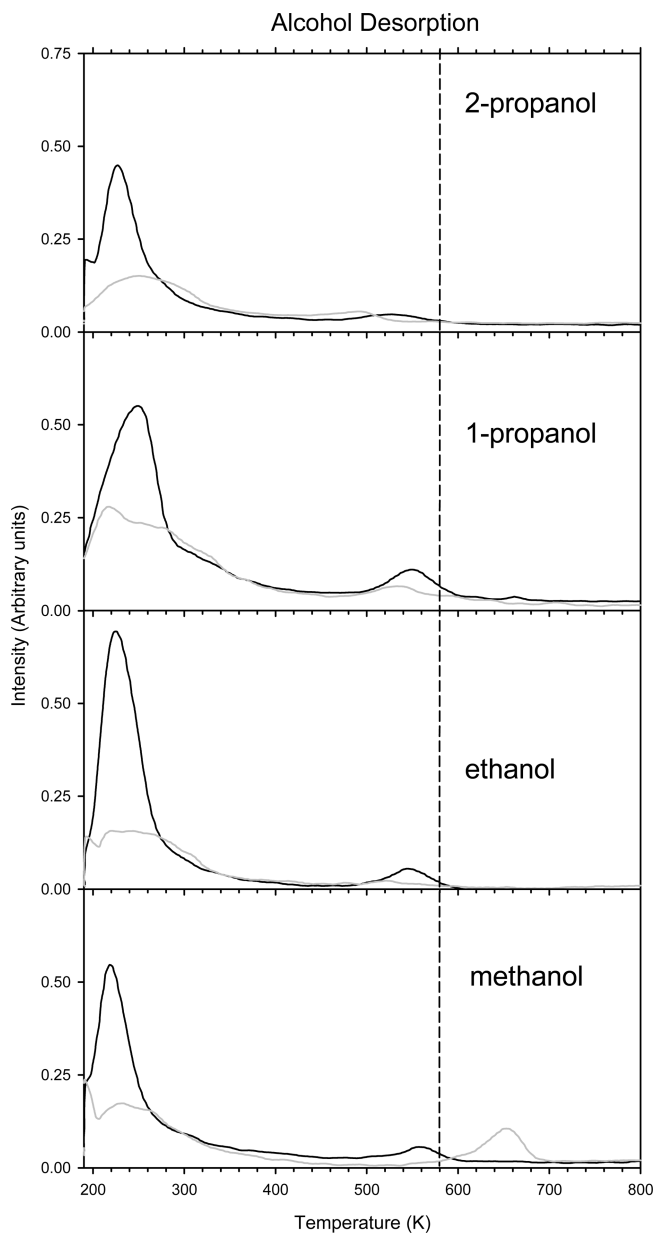
tion increases the photon flux within the analysis area by more than a factor of 10 compared with previous studies. Additional details of experimental equipment, procedures, and parameters for sXPS and TPD have been reported elsewhere.<sup>9,10</sup>

CeO<sub>2</sub>(111) films were grown in situ by Ce vapor deposition onto a Ru(0001) surface at 700 K under an oxygen atmosphere. The procedure has been reported previously.<sup>13</sup> Reduced CeO<sub>x</sub>(111) films were produced by exposing the CeO<sub>2</sub>(111) surfaces to methanol above the methoxy decomposition temperature.<sup>9</sup> The typical treatment was to expose the surface to the equivalent of ca. 100 L of methanol at 700 K. A directed gas doser was used to minimize the total pressure rise in the vacuum chamber.<sup>14</sup> This method resulted in highly reproducible reduced oxidation states. The Ce oxidation state was determined using XPS of the Ce 3d and Ce 4d regions at ORNL and Beamline U12a, respectively.<sup>12</sup> Representative Ce 3d spectra for the initial CeO<sub>2</sub>(111) surface and the reduced CeO<sub>x</sub>(111) surface are shown in Figure 1. We estimate that the reduced surface is 65(±5)% Ce<sup>3+</sup> (CeO<sub>1.67</sub>(111)).

Methanol (99.8%), ethanol (99.5%), 1-propanol (99.7%), and 2-propanol (99.5%) were obtained from Sigma Aldrich. The alcohols were dried over molecular sieves to remove any latent water. At beamline U12a, the adsorbates were introduced to the UHV chamber by way of a variable leak valve using a “backfilling” method. At ORNL, the adsorbate exposure was achieved using a well-calibrated, high-precision effusive gas doser.<sup>14</sup> The flux was estimated to be ca.  $1 \times 10^{14}$  molecules cm<sup>-2</sup> s<sup>-1</sup> based on the calibration method proposed by Liu et al.<sup>15</sup> so that the typical exposure was ca.  $5 \times 10^{15}$  molecules cm<sup>-2</sup>.

### 3. Results

**3.1. TPD.** Methanol, ethanol, 1-propanol, and 2-propanol were adsorbed on the ceria films at 190 K. This temperature is above the multilayer desorption temperature for the various alcohols but below the lowest chemisorbed desorption temperature that was previously observed for methanol,<sup>9</sup> and the exposure was sufficient to saturate the chemisorbed layer. The TPD spectra were then recorded at a heating rate of 2 K/s. The desorption of the alcohol, aldehyde/ketone, alkene, H<sub>2</sub>, and water products are presented in Figures 2–6, respectively. These were the only products detected except for CO, and this was only produced from methanol.<sup>9</sup> In particular, we did not detect alkynes, alkanes, ethers, or CO<sub>2</sub>. Combination products with more carbon than the parent alcohol or smaller products, such as aldehydes, alcohols, or alkenes, with fewer carbons than the parent alcohol were also not observed.



**Figure 2.** TPD of alcohols desorbed from methanol, ethanol, 1-propanol, and 2-propanol adsorbed at 190 K on fully oxidized CeO<sub>2</sub>(111) (solid black line) and 65% reduced CeO<sub>1.67</sub>(111) (gray line). The dashed line is to aid in the comparison of peak positions.

1-Propanol, ethanol, and methanol were monitored at mass 31, 2-propanol at mass 45, propene at mass 41, ethylene at mass 27, propanal and acetaldehyde at mass 29, formaldehyde at mass 30, acetone at mass 43, H<sub>2</sub> at mass 2, and water at mass 18. The contribution from the fragments of the parent alcohols was subtracted from the alkene, aldehyde, and ketone fragments. The intensities for these products at these masses were scaled according to the method described by Ko et al.<sup>16</sup> This method is based on the ionization probability of the molecules, the fragmentation in the mass spectrum, and the response of the analyzer to fragments with various masses. These parameters are only estimates; however, the scaling results in spectra that, at least qualitatively, more accurately reflect the relative intensities of the respective products.

On fully oxidized CeO<sub>2</sub>(111), the parent alcohols all show an intense desorption peak between 200 and 250 K (Figure 2, black lines). There are small differences in the peak desorption temperatures with methanol < ethanol, 2-propanol < 1-propanol.

The intensities of these low-temperature desorption states are similar for the four alcohols. All of the alcohols also have a weaker desorption state that occurs between 500 and 600 K. The peak temperature is near 550 K for methanol, ethanol, and 1-propanol. The intensities for these alcohols are also similar. The intensity for 2-propanol is much weaker, however, and shifts down to near 530 K.

On reduced  $\text{CeO}_{1.67}(111)$  (Figure 2, gray lines), the low-temperature peak for all of the alcohols is greatly attenuated and appears as a broad desorption state from 200 to 350 K. For ethanol and propanol, the higher-temperature state is also attenuated and shifts toward lower temperature compared with the oxidized surface. The intensity of the high-temperature state for methanol increases, however, and the peak shifts from 560 to 650 K.

The dehydrogenation products are formaldehyde, acetaldehyde, propanal, and acetone for methanol, ethanol, 1-propanol, and 2-propanol, respectively. The desorption of these products is shown in Figure 3. The dehydrogenation products all desorb above 500 K.

On the oxidized  $\text{CeO}_2(111)$  surface, the desorption temperatures of the dehydrogenation products are similar to those of the alcohol products that occur in the same temperature range (compare the black lines in Figures 2 and 3). The dehydrogenation products are generally slightly more intense than the alcohol desorption, however, and their desorption profiles are also broader with a prominent lobe appearing near 580 K. As with the alcohol desorption, the desorption intensity appears to increase with chain length with propanal > acetaldehyde > formaldehyde. However, 2-propanol produced relatively little acetone.

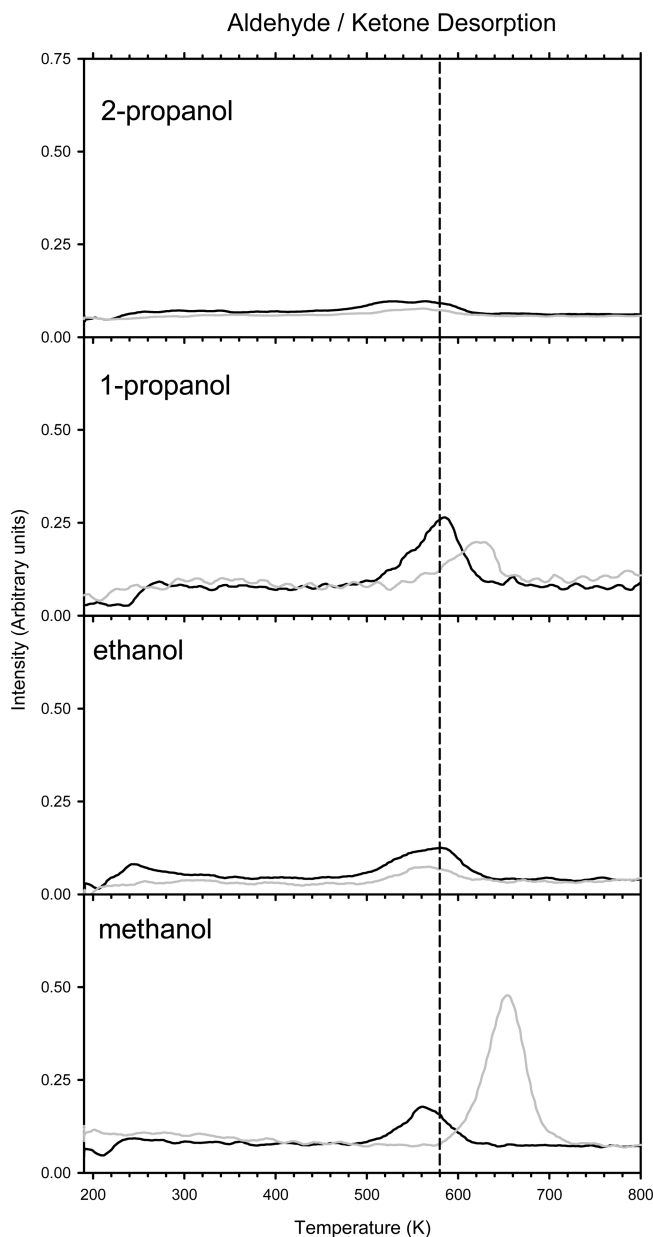
On reduced  $\text{CeO}_{1.67}(111)$  (Figure 3, gray lines), the intensity of the dehydrogenation products decreases for the  $\text{C}_2$  and  $\text{C}_3$  alcohols but increases for methanol compared with the oxidized surface. The temperature at which the product is produced increases for methanol and 1-propanol but remains largely unchanged for ethanol and 2-propanol.

The dehydration products, ethylene and propene, are shown in Figure 4. There is no analogous product from methanol as all of the C-containing products also contain O. On the oxidized surface (black lines) there is considerably more propene produced by 2-propanol than by 1-propanol. The amount of alkene produced by ethanol and 1-propanol is similar. On the reduced surface, the alkene intensities increase for all of the alcohols but the relative increase is greater for 1-propanol and ethanol than for 2-propanol. Between the oxidized and reduced surfaces, the alkene desorption temperature decreased for ethanol and 2-propanol but remained largely unchanged for 1-propanol.

Acetylene or propyne were not detected under any conditions. This was confirmed by monitoring the relative intensities of masses 26, 27, and 28 for ethanol and masses 39, 40, and 41 for the propanols.

In principle, the dehydrogenation and dehydration products should correlate with the formation of  $\text{H}_2$  and  $\text{H}_2\text{O}$ , respectively. However, because ceria is a reducible material, the loss of  $\text{H}_2$  or  $\text{H}_2\text{O}$  from the adsorbate will be convoluted with the gain or loss of O from the substrate.

$\text{H}_2$  and  $\text{H}_2\text{O}$  desorption are shown in Figures 5 and 6, respectively. Very little  $\text{H}_2$  is detected following alcohol reaction on the oxidized surface (Figure 5, black lines). The only significant  $\text{H}_2$  peak is seen from 2-propanol at 580 K. Conversely, almost no water is produced from the reaction of alcohols on reduced  $\text{CeO}_{1.67}(111)$  (Figure 6, gray lines). This suggests that, regardless of whether the alcohol exhibits

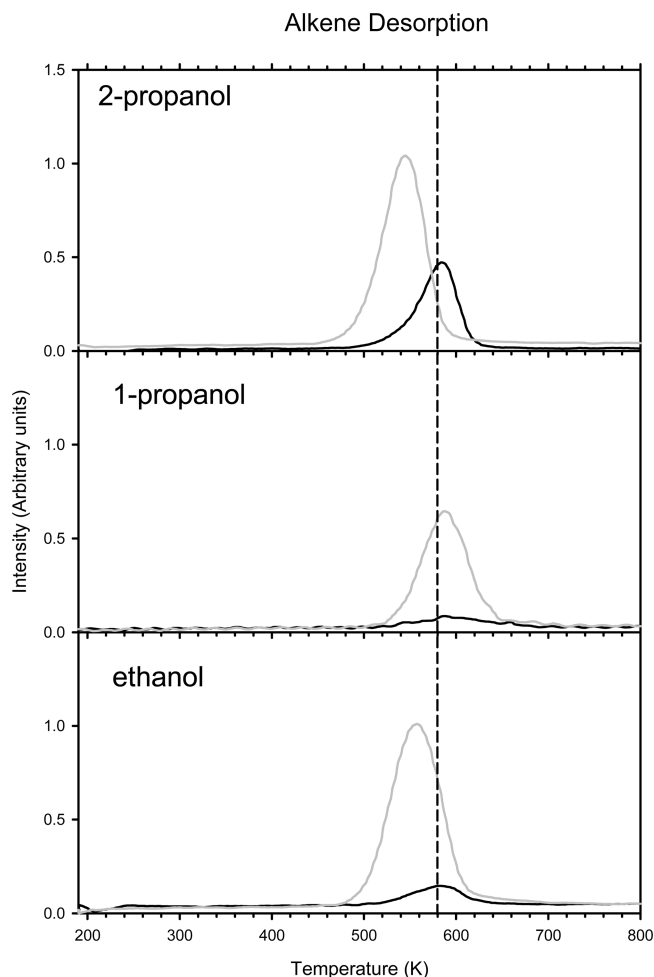


**Figure 3.** TPD of formaldehyde, acetaldehyde, propanal, and acetone produced by methanol, ethanol, 1-propanol, and 2-propanol, respectively, adsorbed at 190 K on fully oxidized  $\text{CeO}_2(111)$  (solid black line) and 65% reduced  $\text{CeO}_{1.67}(111)$  (gray line). The dashed line is to aid in the comparison of peak positions.

dehydration or dehydrogenation, the resulting product is predominantly  $\text{H}_2\text{O}$  from oxidized ceria due to the removal of O from the substrate and  $\text{H}_2$  from reduced ceria due to the gain of O by the substrate.

Most of the water from  $\text{CeO}_2(111)$  (Figure 6, black lines) is produced at low temperature near 220 K. As previously reported,<sup>9</sup> this peak is not due to water contamination in the alcohol adsorbates nor due to a cracking fragment of the alcohols. There are also indications, clearly evident for 1-propanol, of water desorption near 580–600 K.

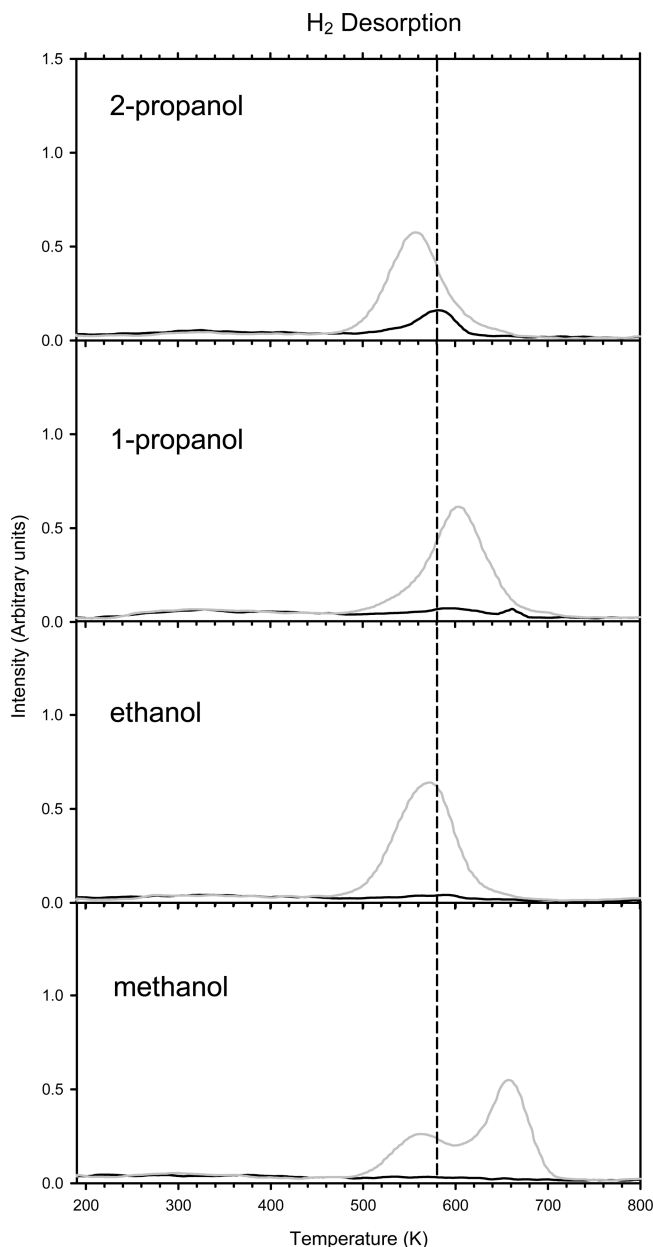
The  $\text{H}_2$  desorption temperatures from reduced  $\text{CeO}_{1.67}(111)$  coincide with the aldehyde, acetone, and alkene desorption temperatures. This suggests that the desorption between 540 and 600 K is reaction-limited and results from the reaction/decomposition of surface intermediates. The exception to this pattern is methanol where  $\text{H}_2$  desorption at 560 K does not coincide with the other desorption products. A  $\text{H}_2$  peak near



**Figure 4.** TPD of ethylene, propene, and propene produced by ethanol, 1-propanol, and 2-propanol, respectively, adsorbed at 190 K on fully oxidized CeO<sub>2</sub>(111) (solid black line) and 65% reduced CeO<sub>1.67</sub>(111) (gray line). The dashed line is to aid in the comparison of peak positions.

550 K has been shown to result from the reaction of OH groups on the surface.<sup>17</sup> Presumably, recombination of surface hydroxyls also occurs with the other alcohols, but the reaction occurs at approximately the same temperature as the reaction of the adsorbed alkoxy species.

**3.2. sXPS.** Methanol, ethanol, and 2-propanol were adsorbed at 185 K and then annealed to 300 K. 1-Propanol was not studied. The three alcohols were all examined over a 2 week period. This ensured that (a) possible sensitivity variations due to changes in the photon flux monitor or the electrostatic analyzer were minimized and (b) similar CeO<sub>2</sub>(111) surface preparations and degrees of reduction were utilized. The spectra were recorded after annealing to 300 K in order to minimize X-ray exposure, although only a small amount of X-ray damage was observed for the alcohols. In other studies, spectra were recorded immediately after exposure at 185 K and, subsequently, after annealing to various temperatures to determine if the surface species changed as a function of temperature. These studies indicated no significant qualitative changes with temperature up to the product desorption temperature. On oxidized CeO<sub>2</sub>(111), the total C 1s intensity decreased by ca. 50% between 185 and 300 K for all alcohols, whereas the intensity decreased by a much smaller amount on reduced ceria. This is consistent with the greater amounts of alcohol that desorb at low temperature from the oxidized surface compared to the reduced surface (Figure 2).

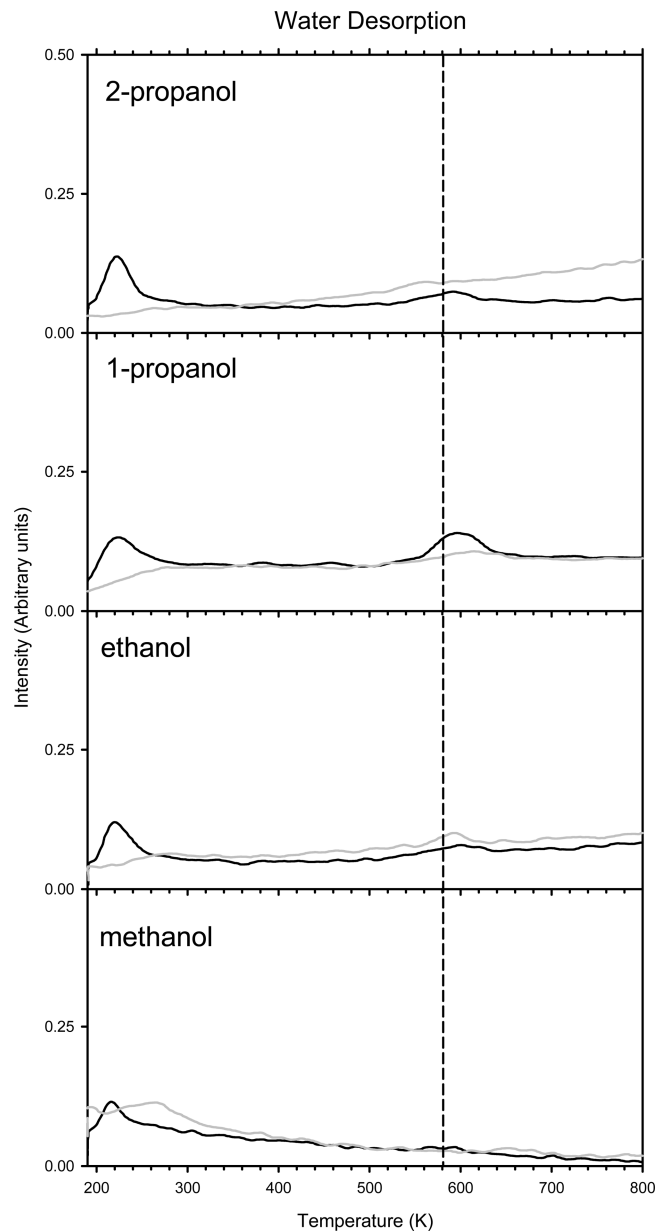


**Figure 5.** TPD of H<sub>2</sub> produced by methanol, ethanol, 1-propanol, and 2-propanol adsorbed at 190 K on fully oxidized CeO<sub>2</sub>(111) (solid black line) and 65% reduced CeO<sub>1.67</sub>(111) (gray line). The dashed line is to aid in the comparison of peak positions.

The C 1s spectra on CeO<sub>2</sub>(111) and CeO<sub>1.67</sub>(111) are shown in Figures 7 and 8, respectively. The C 1s spectra of the alcohols can be characterized by two prominent features that are associated with either an alkoxy C and/or an alkyl carbon. Methanol contains only the methoxy C, so its spectra can be used to assign the nominal C 1s peak position for the alkoxy species. On CeO<sub>2</sub>(111) (Figure 7), this peak is at ca. 287 eV, which is consistent with our previous study of methanol on ceria.<sup>9</sup> A second peak is evident for ethanol and 2-propanol at slightly less than 286 eV. A third, weak feature is evident near 290 eV. This is assigned to a carboxylate species resulting from X-ray damage. A correlation between the intensity of this feature and X-ray exposure was demonstrated by varying the exposure duration and moving to different spots on the sample. The Ce 4s peak also occurs near 290 eV, as shown in the spectrum from the clean surface at the bottom of Figure 7.

On the reduced CeO<sub>1.67</sub>(111) surface (Figure 8), the same two characteristic features are evident but they are systematically



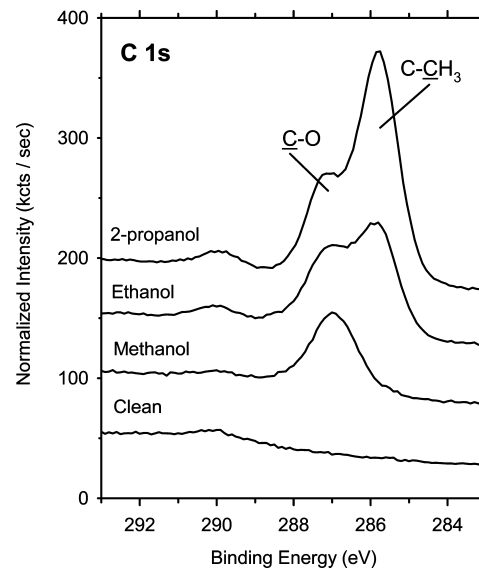


**Figure 6.** TPD of  $\text{H}_2\text{O}$  produced by methanol, ethanol, 1-propanol, and 2-propanol adsorbed at 190 K on fully oxidized  $\text{CeO}_2(111)$  (solid black line) and 65% reduced  $\text{CeO}_{1.67}(111)$  (gray line). The dashed line is to aid in the comparison of peak positions.

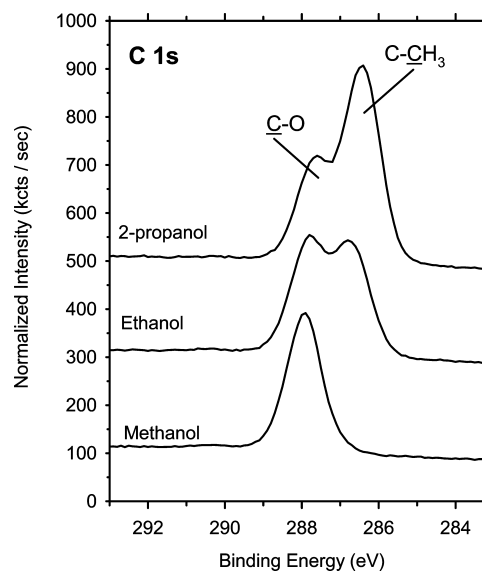
shifted by ca. 1 eV to higher binding energy. As observed in many other cases, the peak positions of nominally the same species are shifted by ca. 1 eV on a reduced  $\text{CeO}_x(111)$  surface compared with the oxidized  $\text{CeO}_2(111)$  surface.<sup>9,11,18,19</sup> Whereas the alkoxy peak is in the same position for the three alcohols (288 eV), the methyl peak position is shifted more for ethoxy (286.8) compared with 2-propanol (286.5). The carboxylate feature is weak or nonexistent in Figure 8. This is consistent with previous studies where X-ray damage was more evident on the oxidized surface compared with the reduced surface.<sup>11,20</sup>

The total C 1s intensities suggest that the surface coverages on the oxidized surface are similar. On the oxidized surface (Figure 7), the total relative C 1s intensity (not counting the feature near 290 eV) is methoxy:ethoxy:2-propoxy = 1.0:2.0:2.7. On the reduced surface (Figure 8), the variation is more statistically significant. The ratio is 1.0:1.5:2.1.

The expected peak intensity ratios between the alkoxy and methyl groups in ethoxy (1:1) and 2-propoxy (1:2) are correct



**Figure 7.** C 1s sXPS of methanol, ethanol, and 2-propanol adsorbed on fully oxidized  $\text{CeO}_2(111)$  at 185 K and then annealed to 300 K.

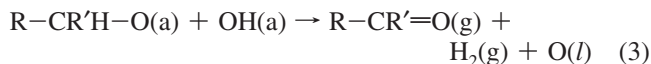
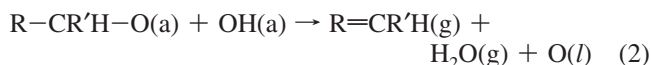
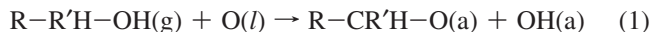


**Figure 8.** C 1s sXPS of methanol, ethanol, and 2-propanol adsorbed on 65% reduced  $\text{CeO}_{1.67}(111)$  at 185 K and then annealed to 300 K.

on the reduced surface (Figure 8). However, on the oxidized surface, the methyl group intensities appear to be greater than they should be. This may be due to the X-ray damage that converts the alkoxy to a carboxylate. If hydrogen is ejected so that ethoxy is converted to acetate, for example, the intensity of the ethoxy peak would be diminished but the methyl peak would remain the same. The methyl groups may also attenuate the alkoxy groups, which are closer to the surface.

#### 4. Discussion

The reaction pathways of  $\text{C}_1$ – $\text{C}_3$  alcohols on oxidized and reduced  $\text{CeO}_x(111)$  can primarily be understood in terms of dissociative adsorption to produce alkoxy and hydroxyl (reaction 1), followed by dehydration (reaction 2) or dehydrogenation (reaction 3) to produce alkenes or aldehydes/ketones, respectively. There is no evidence of products resulting from either the formation of new C–C or C–O bonds (coupling) or breaking C–C bonds.



In these reactions, (g) refers to gas-phase species, (a) refers to adsorbed species, O(l) is lattice oxygen, and R and R' may indicate to either an alkyl group/chain or hydrogen. Note that, if both R and R' are hydrogens (methanol), then reaction (2) is not applicable.

The formation of alkoxy species on both the oxidized and the reduced surfaces is evident in the C 1s xPS spectra (Figures 7 and 8). The intensity of the alkoxy-related peak is essentially the same for the three alcohols studied, indicating that the adsorbate coverage is not limited by adsorbate–adsorbate interactions. We have previously shown for methanol that the methoxy coverage near 200 K is ca. 8 nm<sup>−2</sup> on CeO<sub>2</sub>(111).<sup>9</sup> This is equal to the density of the Ce<sup>4+</sup> cations in the CeO<sub>2</sub>(111) surface and suggests that alkoxy adsorbs by adsorbing on the under-coordinated Ce<sup>4+</sup> sites. These sites are the seven-coordinated Ce<sup>4+</sup> cations located in the second layer beneath the O-terminated CeO<sub>2</sub>(111) surface. It has been shown by STM that there are relatively few O vacancies on the fully oxidized surface<sup>21,22</sup> and they would not provide sufficient adsorption sites for the amount of alkoxy that adsorbs.

Ethanol and 1-propanol adsorption on ZnO(0001) produced alkoxides that were oxidized by lattice O to form carboxylates.<sup>6</sup> The carboxylates led to nonselective oxidation products (CO and CO<sub>2</sub>) that were not observed in this study. Carboxylates are evident near 290 eV on the oxidized surface (Figure 7), but they were primarily attributed to X-ray-induced processes. Some of the carboxylates may have been thermally generated, but they appear to be minor contributions on CeO<sub>2</sub>(111), and nonexistent on reduced CeO<sub>1.67</sub>(111), and will not be considered further.

On the fully oxidized CeO<sub>2</sub>(111) surface, there is a clear difference between the primary and secondary alcohols with respect to the selectivity between the two reaction pathways, as shown in Table 1. This is most evident in the propanol isomers. The secondary alcohol, 2-propanol, produces propene almost exclusively through dehydration, whereas the primary alcohol, 1-propanol, exhibits predominantly dehydrogenation, yielding twice as much propanal compared with propene. Ethanol, also a primary alcohol, produces similar amounts of ethylene and acetaldehyde.

Most examples reported on well-characterized, single-crystal surfaces have shown an overwhelming propensity toward one path or the other. On TiO<sub>2</sub>(110), only primary alcohols produce any aldehyde products and the alkene selectivity is still ca. 90%.<sup>23</sup> Similar results were obtained on {011}-faceted TiO<sub>2</sub>(001).<sup>8</sup> Conversely, reaction of 1-propanol on CuO<sub>2</sub>(100) had an aldehyde selectivity of ca. 70–80% (depending on coverage).<sup>24</sup> Similarly, ZnO(0001)–Zn produced a 76% aldehyde selectivity for ethanol<sup>6</sup> and 100% propanol or acetone selectivity for 1-propanol<sup>6</sup> or 2-propanol,<sup>25</sup> respectively. These materials generally show an increase in selectivity, toward either dehydration or dehydrogenation, as chain length or branching increases. CeO<sub>2</sub>(111) does not follow this simple pattern. An increase in chain length from ethanol to 1-propanol increases the selectivity toward dehydrogenation, whereas branching from a primary to a secondary alcohol reverses the selectivity to almost exclusively dehydration.

**TABLE 1: Selectivity for Dehydration versus Dehydrogenation for Ethanol, 1-Propanol, and 2-Propanol on Oxidized and Reduced CeO<sub>x</sub>(111) As Determined by the Ratio of the Alkene Product Divided by the Aldehyde/Ketone Product in TPD**

	oxidized CeO <sub>2</sub> (111)	reduced CeO <sub>x</sub> (111)
ethanol	1.0	19.3
1-propanol	0.5	5.6
2-propanol	9.2	31.3

The selectivity on CeO<sub>2</sub>(111) is somewhat consistent with the variation in dehydration reaction temperature observed for various alcohols on TiO<sub>2</sub>(110).<sup>23,26</sup> On TiO<sub>2</sub>(110), the alkene desorption temperature decreased either as the alkyl chain length increased or as more alkyl substituents were bonded to the α-carbon. This was attributed to the so-called inductive effect where the electron-donating alkyl groups stabilize the transition state for C–O bond cleavage and thereby lower the activation barrier. On TiO<sub>2</sub>(110), this manifests itself in lowering the desorption temperature. On CeO<sub>2</sub>(111), there is not a clear trend in the reaction temperature but the inductive effect is evident in the alkene selectivity between 2-propanol and 1-propanol (Table 1). The trend is not evident in the selectivity difference between ethanol and 1-propanol, however, as seen on TiO<sub>2</sub>(110); there is little difference between these two alcohols.<sup>26</sup>

UO<sub>2</sub>(111) displays a selectivity for ethanol that is similar to CeO<sub>2</sub>(111).<sup>27</sup> These authors showed a correlation between the heats of formation, dielectric constant, and the Madelung potentials of various oxides and their dehydrogenation/dehydration selectivity. They reported that oxides with greater heats of adsorption, dielectric constants, or Madelung potentials promoted dehydration reactions. The heat of formation for CeO<sub>2</sub> is similar to that for UO<sub>2</sub>, but the dielectric constant is much lower.<sup>28</sup> A clear correlation for CeO<sub>2</sub> is, therefore, not evident. Reactions involving 1-propanol versus 2-propanol were not reported on UO<sub>2</sub>(111).

There are some broad similarities between the reactions of these alcohols on CeO<sub>2</sub>(111) and some of these other surfaces. The predominant adsorption process is dissociative adsorption (reaction 1) leading to adsorbed alkoxy and hydroxyl. This adsorption occurs at O-coordination vacancies on the oxide surface cations.<sup>29</sup> At relatively low temperatures, recombination occurs, leading to alcohol desorption (the reverse of reaction 1). However, a competing reaction is often observed (reaction 4), which is the disproportionation of surface hydroxyl groups, leading to desorbed water and a surface oxygen vacancy (V<sub>O</sub>).



These low-temperature processes are evident with all of the alcohols in this study (Figures 2 and 6) and occur near 220 K. Similar to what was observed on ZnO(0001)<sup>6</sup> and {110}-faceted TiO<sub>2</sub>(001),<sup>8</sup> roughly 50% of the adsorbed alcohol is removed through recombination at low temperature. The remaining alkoxy is stabilized by either (a) the lack of surface H that was removed by reaction 4 or (b) the creation of O vacancies (V<sub>O</sub>) that are more stable adsorption sites for the alkoxy.<sup>30</sup> A unique feature of CeO<sub>2</sub>(111) is that alcohol recombination and water desorption occur at a much lower temperature than have been observed on these other surfaces.<sup>6,8</sup>

Decomposition of the alkoxys, leading to alkenes, aldehyde, and ketones, generally occurs between ca. 500 and 600 K. On TiO<sub>2</sub>(110), where dehydration predominates, the alkene product

desorption systematically shifted toward lower temperatures as the chain length is increased or more alkyl substituents were added to the  $\alpha$ -carbon.<sup>23</sup> Conversely, on ZnO(0001), where dehydrogenation dominates, the aldehyde desorption temperature decreased between ethanol and 1-propanol.<sup>6</sup> A systematic trend in the desorption temperature for either dehydrogenation or dehydration is not evident on CeO<sub>2</sub>(111). The peak desorption temperatures for the aldehydes produced by methanol, ethanol, and 1-propanol all occur near 560–580 K (Figure 3). The desorption peaks are broad enough that subtle shifts cannot be detected. The acetone desorption from 2-propanol is weak, but the centroid of the desorption envelope may be slightly lower than the propanal desorption from 1-propanol. Similarly, the alkene desorptions (Figure 4) all occur near 590 K. On CeO<sub>2</sub>(111) all of the alcohols appear to decompose at about the same temperature. Therefore, unlike what has been attempted on some of these other surfaces, we cannot draw any conclusion regarding selectivity based the relative strengths of C–O or C–H bonds between the alcohols.

The formation of aldehyde or alkene products implies the production of H<sub>2</sub> or H<sub>2</sub>O to balance the loss of hydrogen. This is evident in the TPD results in Figures 5 and 6; however, alkene or aldehyde production does not necessarily lead to the observation of H<sub>2</sub>O or H<sub>2</sub>, respectively. This is because the H and O in the alcohols interact with the O or the O vacancies, respectively, on the surface of the ceria.

All of the alcohols produce water between 200 and 220 K on oxidized ceria (Figure 6). It was previously shown with methanol that this was the result of the H in the hydroxyl of the alcohol reacting with the O in the ceria.<sup>9</sup> The C<sub>2</sub> and C<sub>3</sub> alcohols behave similarly. Methanol then produces formaldehyde and methanol near 560 K. The production of an excess of O-containing products results in the reduction of the ceria. Similarly, the formation of water and aldehydes, with little or no alkenes and virtually no H<sub>2</sub> from ethanol and 1-propanol, results in the reduction of the ceria. This is evident in the Ce 3d XPS, which shows a gradual buildup of Ce<sup>3+</sup> as repeated adsorption/desorption cycles of the primary alcohols are run (data not shown).

2-Propanol produces primarily water at 220 K and propene at 590 K. The O in the reactant and products is essentially balanced, and repeated adsorption/desorption cycles of 2-propanol do not lead to reduction of the ceria. Although the net reaction is dehydration of the 2-propanol, the water desorption at low temperature results from H reacting with the O from the ceria. The H lost by the decomposition of 2-propoxide to propene is contained in H<sub>2</sub> and a small amount of H<sub>2</sub>O near 580 K. 2-Propanol was the only alcohol that produced a significant amount of H<sub>2</sub> from the fully oxidized surface.

On a reduced surface, the selectivity for ethanol and 1-propanol shifts toward dehydration (Table 1), the alkene products increase significantly (Figure 4, gray lines), and the aldehyde products decrease (Figure 3, gray lines). The absolute amount of propene from 2-propanol also increases. The reduced ceria surface consists of a mixture of Ce<sup>3+</sup> and Ce<sup>4+</sup> and numerous O vacancies, which compete with the aldehyde product for the O atom in the adsorbate. For ethanol and 2-propanol, not only does the alkene fraction increase but also the desorption temperature decreases. Conversely, for methanol and 1-propanol, the aldehyde desorption temperatures increase. The selectivity may, therefore, be related to the relative strength of the C–O and Ce–O bonds. As the Ce–O bond strength increases on reduced ceria, it becomes more difficult to break the Ce–O bond

to form the aldehydes; likewise, it becomes easier to break the C–O bond to form alkenes and oxidize the substrate.

The increased surface O stability is also reflected in the water and H<sub>2</sub> desorption. Water desorption essentially disappears on the reduced surface (Figure 6, gray lines), whereas H<sub>2</sub> becomes intense (Figure 5, gray lines). The surface hydroxyls are stable and decompose by desorbing H<sub>2</sub> rather than extracting O from the surface through H<sub>2</sub>O desorption (reaction 4). The formation of alkenes and H<sub>2</sub>, but no water, on the reduced surface leads to oxidation of the reduced ceria by ethanol and the propanols.

Methanol is a unique case because it does not have any C–C bonds and, therefore, cannot produce any stable products upon breaking the C–O bond (note that no coupling products were detected). The methanol, formaldehyde, and CO desorption temperatures directly correlate with the increasing strength of the O–Ce bond. The H<sub>2</sub> desorption also divides into two distinct peaks. The lower-temperature peak at 560 K comes from the decomposition of surface OH that was formed during the methanol adsorption below 200 K.<sup>9,17</sup> The high-temperature peak at 660 K accompanies the decomposition of the methoxy. All of the alcohols should have H<sub>2</sub> desorption near 560 K because they all produced surface OH upon adsorption. Because ethanol and 2-propanol do not produce acetaldehyde or acetone above 600 K, the H<sub>2</sub> from the hydroxyl and alkoxy decomposition reactions overlap. The H<sub>2</sub> desorption from 1-propanol is shifted to slightly higher temperature compared with the other alcohols, reflecting the increased desorption temperature of propanal on the reduced surface.

## 5. Conclusions

The C<sub>1</sub>–C<sub>3</sub> alcohols react readily on oxidized and reduced CeO<sub>x</sub>(111). They form alkoxy and hydroxyl species at low temperature. On the fully oxidized surface, about half of the alkoxides recombine with OH near 200 K to produce gaseous alcohol. The remainder of the surface hydroxyl is removed as water, leaving stable alkoxys on the surface. The remaining alkoxys react above 550 K. The primary alcohols produce primarily aldehydes and produce a net reduction of the ceria substrate. The secondary alcohol, 2-propanol, produces primarily propene with no net change in the ceria oxidation state.

Adsorption on reduced ceria results in less alkoxy recombination at low temperature with substantially more selective decomposition products produced at high temperature. Reduction of the ceria substrate also shifts the selectivity toward dehydration with ethanol and 1-propanol producing primarily ethylene and propene. The alkene desorption temperature moves to a lower temperature compared with the reaction on the oxidized substrate, whereas the aldehyde desorption shifts to a higher temperature. This indicates that it is easier to break the C–O bond on the reduced surface, whereas it is more difficult to break the O-substrate bond.

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