Adsorption and Reaction of Acetone over CeOx(111) Thin Films

4 AUTHORS, INCLUDING:

Sanjaya D. Senanayake
Brookhaven National Laboratory
108 PUBLICATIONS **1,738** CITATIONS

SEE PROFILE

Wesley Gordon
United States Army
15 PUBLICATIONS **214** CITATIONS

SEE PROFILE

David Mullins
Oak Ridge National Laboratory
139 PUBLICATIONS **3,859** CITATIONS

SEE PROFILE

Adsorption and Reaction of Acetone over CeO$_x$(111) Thin Films

S. D. Senanayake, W. O. Gordon, S. H. Overbury, and D. R. Mullins*

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6201

This study reports the interaction of acetone (CH_3COCH_3), the simplest ketone, with well ordered $CeO_2(111)$ thin film surfaces. The fully oxidized $CeO_2(111)$ surface shows a weak interaction with acetone with the sole desorption product (TPD) being acetone at 210 K. The chemisorbed molecule binds to the surface as the η_1-acetone species rather than through a bridge-bonded dioxy-configuration. Exposure of a $CeO_2(111)$ surface to acetone at 600K removes oxygen as CO and results in the conversion of Ce^{4+} to Ce^{3+}. Acetone chemisorbs strongly on reduced $CeO_{2-x}(111)$ with molecular acetone desorbing near 500 K. Decomposition also occurs with H_2 desorbing between 450 and 600 K and C reacting with O in the ceria to desorb above 650 K. A stable species exists from 200 to 500 K on the reduced surface that has three unique types of C. High resolution C 1s XPS spectra indicate these are Ce−CH$_2$, C−$\underline{C}$H$_3$ and C−O species. C k-edge NEXAFS indicates the presence of C=C and C=O bonds. It is postulated that the intermediate is a carbanion bonded through both O and C atoms to Ce cations.

1. Introduction

Cerium oxide surfaces have been the recent focus of numerous studies as a result of unique oxygen storage properties that promote their use in many redox chemical processes.[1] Ceria possesses two easily accessible higher oxidation states (Ce^{4+} and Ce^{3+}). Samples can exhibit a mixture of oxidation states within a stoichiometry ranging from $CeO_{1.5}$ to CeO_2. The relative amounts of Ce^{3+} and Ce^{4+} can be determined by several electron spectroscopic methods.[2] As Ce is converted between the two oxidation states, the lattice oxygen can be readily donated to surface reactants or, alternatively, O can be removed from reactants and incorporated into O^{2-} vacancies in reduced CeO_x.

Highly ordered thin films of CeO_2/CeO_{2-x} (111) can be either oxidized or reduced by simple C_1-oxygenates depending on the molecule and the initial oxidation state of the ceria. Methanol reduces $CeO_2(111)$ leading to the formation of formaldehyde and water,[3] while formaldehyde only decomposes to CO and H_2 resulting in no net change in the Ce oxidation state.[4] Formic acid demonstrated a dual nature being oxidized to CO_2 and H_2O on $CeO_2(111)$ and reduced to CO and H_2 on reduced $CeO_{2-x}(111)$.[5] Reduced ceria was also shown to be readily oxidized by NO liberating N_2.[6]

In this work, we present the first study of an O-containing molecule with more than one C atom over a well defined cerium oxide thin film surface. Acetone is the simplest of the ketone molecules with a central carbonyl component flanked by two methyl groups (CH_3COCH_3). We might anticipate that acetone will react in a manner similar to formaldehyde ($H_2C=O$). The key question in this study is how the pendant methyl groups interact with the surface or promote interactions between adsorbates.

The adsorption and reaction of acetone have previously been studied over several single crystal metal oxide surfaces including $ZnO(0001)−Zn$ and $ZnO(000\bar{1})−O$,[7] $TiO_2(110)$,[8] $TiO_2(001)$,[9] and $UO_2(111)$.[10] Acetone was unreactive on the O-terminated $ZnO(000\bar{1})$ surface but totally decomposed above 700 K to CO and CO_2 on the Zn-terminated $ZnO(0001)$ surface.

Henderson[8] showed that on the $TiO_2(110)$ surface acetone adsorbed molecularly via an η_1-acetone intermediate that is bonded to the metal cations via the carbonyl oxygen. No decomposition products were produced from either an oxidized or a reduced surface. However, he also reported that it is possible to make acetates from acetone via photo-oxidation over the same surface.[11] This reaction is reported to proceed via an "acetone-oxygen" surface intermediate that ejects a methyl radical to create acetate on the surface which decomposes further to give ketene.

In the case of $TiO_2(001)$, both dehydration to propylene and reductive coupling to 2,3-dimethyl-2-butene were observed.[9] Surface oxygen vacancies produced a 10-fold increase in the yield of these products compared to desorption. The reductive coupling was proposed to occur through a pinacolate intermediate that arises from aldol condensation of two molecules of acetone.

On $UO_2(111)$, acetone reacts very weakly with the oxidized surface with predominantly acetone and small quantities of dimethyl-2-butene as the visible desorption products.[10] However, upon introduction of surface oxygen defects (oxidation states < U^{4+}) the reaction pathways led to decomposition (CO_2, CO, and H_2O), aldol condensation (4-methyl-3-penten-2-one, 4-methyl-1,3-pentadiene) and traces of cyclization products (trimethylbenzene).

In this work, we will show that on the fully oxidized ceria surface acetone adsorbs weakly and is unreactive. However, unlike formaldehyde, the C=O bond remains intact rather than forming a bridge-bonded O−C−O species on the surface. On reduced ceria, acetone bonds more strongly as a heterocyclic carbanion species. This species either desorbs as acetone or reacts with the ceria to form H_2 and CO.

2. Experimental Section

Experiments were performed in two separate UHV chambers. Soft X-ray photoelectron spectroscopy (sXPS) and near-edge X-ray absorption fine structure spectroscopy (NEXAFS) were

---

* Corresponding author. E-mail: mullinsdr@ornl.gov. Phone: 865-574-2796. Fax: 865-576-5235.

conducted using synchrotron radiation on beamline U12a at the National Synchrotron Light Source (NSLS). Temperature programmed desorption (TPD) was performed in a separate chamber at Oak Ridge National Laboratory (ORNL).

C 1s and O 1s spectra were recorded at photon energies of 400 and 600 eV, respectively. The instrumental resolution was ca. 0.5 eV. The Ce 4d photoemission was used for binding energy calibration using the 122.3 eV satellite feature.[3] Additional details of experimental equipment, procedures, and parameters for NEXAFS, sXPS and TPD have been reported elsewhere.[5]

CeO$_2$(111) and partially reduced CeO$_{2-x}$(111) films were grown in situ by vapor deposition onto a hot Ru(0001) surface (700 K) under an oxygen atmosphere. The procedure has been reported previously.[12] The structure, composition and oxidation state of the CeO$_x$(111) surfaces have been characterized by XPS,[2] low energy ion scattering[12] and scanning tunneling microscopy (STM).[13] Growth of labeled Ce^{18}O$_2$(111) films was achieved by substituting ^{16}O$_2$ with labeled ^{18}O$_2$ obtained from Cambridge Isotopes (>95% isotopic purity). The Ce oxidation state was determined using XPS of the Ce 3d and Ce 4d regions at ORNL and Beamline U12a, respectively.

Acetone was obtained from Mallinckrodt Chemicals (99.8%). Mass spectral analysis showed that the acetone was free of contaminants after several freeze−pump−thaw cycles. At beamline U12a, the adsorbate was introduced to the UHV chamber by way of a variable leak valve using a "back-filling" method. At ORNL the adsorbate exposure was achieved using a well calibrated high precision effusive gas doser.[14] The flux was estimated to be ca. 1×10^{14} molecules cm^{-2} s^{-1} based on the calibration method proposed by Liu et al.[15] A similar flux was also determined by monitoring the rate of decrease of the acetone pressure in the gas reservoir supplying the directed doser.[14]

3. Results

3.1. Acetone Reaction with Fully Oxidized CeO$_2$(111). Acetone interacted weakly with the fully oxidized CeO$_2$(111) surface. The only desorption product was acetone as shown by the solid black lines in Figure 1. Acetone desorption was monitored at Mass 43 which is its most intense cracking fragment. When properly scaled the desorption at Mass 43 was superimposable with the weaker desorption at the parent peak at Mass 58. No H$_2$, CO, H$_2$O, CO$_2$, hydrocarbons, aldehydes, acids, or other ketones were detected. Physisorbed acetone desorbs at ca. 125 K.[8] The acetone exposures in Figure 1 were therefore conducted at 140 K to minimize the contribution from this weakly bound state. Chemisorbed acetone desorbs primarily at 210 K. A more strongly adsorbed state is also evident near 300 K.

C 1s sXPS spectra following the exposure of 8 L (1 L = 10^{-6} Torr s) of acetone on CeO$_2$(111) at 95 K are shown in Figure 2. Following exposure, the C 1s spectrum consists primarily of two features at 286.3 and 289.3 eV which have a relative intensity of ca. 2:1, respectively. These features are associated with the methyl (ca. 286 eV) and carbonyl (ca. 289 eV) carbons in acetone. The ∼3 eV splitting between the two features is very similar to physisorbed acetone observed on other surfaces.[7,16] Upon heating to 150 K most of the physisorbed species has desorbed leaving features at ca. 285.3, 287.9, and 289.5 eV. These features are broad, asymmetric and presumably encompass more than three binding energy states. Upon annealing to 300 K, most of the C-containing species are gone with small features remaining at 286 and 290 eV.
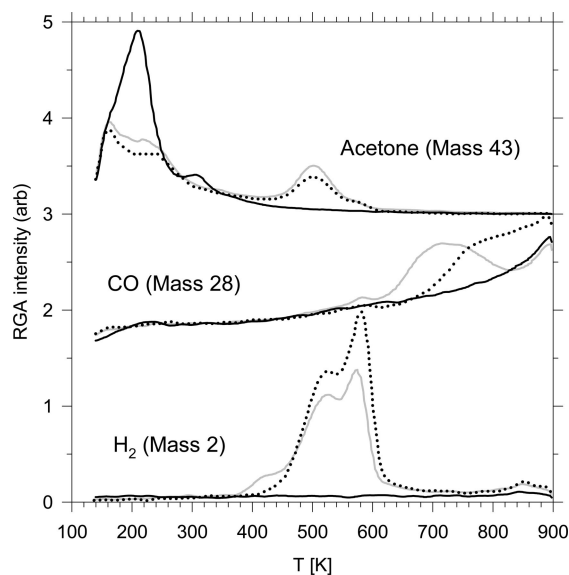

Figure 1. TPD following the adsorption of acetone on oxidized and reduced reduced CeO$_x$(111) at 140 K. The solid line black lines are from fully oxidized CeO$_2$(111), the gray lines are from the first exposure of acetone on reduced CeO$_{1.75}$(111) and the dotted lines are following the fifth exposure/TPD cycle on CeO$_{1.75}$(111).
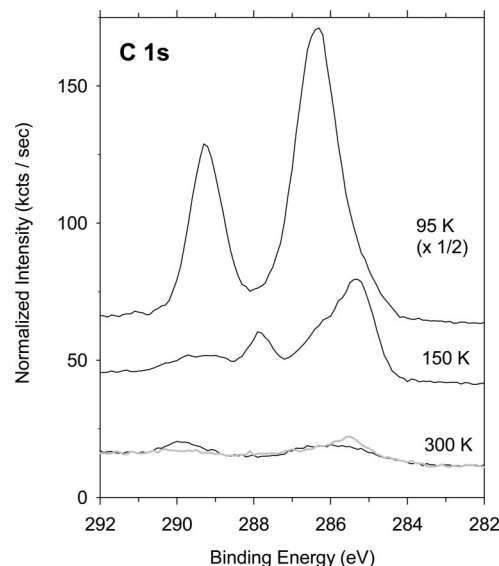

Figure 2. C 1s sXPS spectra following adsorption of acetone on CeO$_2$(111) at 95 K and then annealed as indicated. The gray line was recorded in a separate experiment in which the acetone was adsorbed at 95 K and then immediately annealed to 300 K without exposing the surface to X-rays at lower temperatures.

The sample was tested to determine if X-ray beam damage occurred. The ceria was again exposed to acetone at 95 K but was then annealed to 300 K without exposing it to X-rays. The resulting C 1s spectrum is shown by the gray line in Figure 2 superimposed over the original 300 K spectrum. The feature near 290 eV is greatly diminished while a sharper, more intense peak near 285.5 occurs. This indicates that the peak near 290 eV is the result of beam damage. The X-rays apparently cleave a C−C bond. The CH$_3$CO fragment bonds to a surface O producing an acetate with a C 1s binding energy near 290 eV, and diminishing the intensity of the methyl moiety at 285.5 eV. X-ray damage was also observed in formaldehyde adsorption on CeO$_2$(111) where dioxymethylene was converted to formate.[4]

In Figure 3, the spectrum at 300 K (dark curve) in Figure 2 was subtracted from the spectrum at 150 K to remove the beam
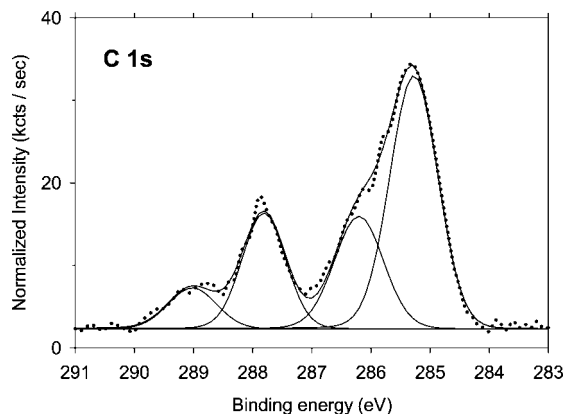
Figure 3. Spectral decomposition of the principal peaks present after annealing acetone adsorbed at 95 K on $CeO_2(111)$ to 150 K. The dotted line is the spectrum at 300 K in Figure 2 subtracted from the spectrum at 150 K in order to remove X-ray induced decomposition products. The solid lines are the best-fit spectral components.

damaged components from the low temperature spectrum. The resulting spectrum was fit with four peaks using the program FitXPS v2.12.[17] The peaks at 286.2 and 289.0 eV have binding energies similar to the large multilayer peaks observed at 95 K and are therefore assigned to a weakly bound state of acetone that does not strongly interact with the surface. The other two features at 285.2 and 287.8 eV are associated with an acetone-like species chemisorbed on the ceria. As observed with the C_1 oxygenates on ceria,[3-5] the chemisorbed species has a lower binding energy than the physisorbed species. The C 1s sXPS can not conclusively identify the chemisorbed adsorbate, however. The acetone could be bonded as either an η_1-acetone intermediate (1) as was proposed on $TiO_2(110)$[8] or as dioxypropylene (2) in a manner analogous to formaldehyde which forms dioxymethylene on $CeO_2(111)$.[4]
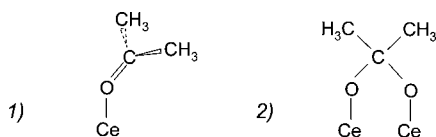
These species can be differentiated by the C k-edge NEXAFS spectra. Figure 4a shows the C k-edge NEXAFS at two different incident angles for a thick layer of acetone adsorbed on $CeO_2(111)$ at 90 K. The spectra are consistent with those recorded from multilayer acetone on Si(100).[18] The most prominent features are the $\pi*$ (C=O) resonance at 286.2 eV and the $\pi*$ (CH$_3$) resonance at 289 eV. The polarization dependence, with the $\pi*$ features more intense at normal incidence, indicates the acetone molecular plane is oriented nearly normal to the surface as was observed on Si(100). The $\pi*$ resonances adsorb light polarized normal to the molecular plane and at normal incidence the polarization vector is oriented parallel to the surface.

The C k-edge NEXAFS recorded after the sample was exposed to acetone at 95 K and then annealed to 175 K to desorb the multilayer acetone is shown in Figure 4b. The $\pi*$ (C=O) resonance is still evident at 286.2 eV. This indicates that the chemisorbed species is not the dioxypropylene species (2). In contrast, when formaldehyde was adsorbed on $CeO_2(111)$ the $\pi*$ (C=O) resonance disappeared in the chemisorbed species leading to the conclusion that dioxymethylene was formed.[4] The intensity of the $\pi*$ (C=O) resonance is the same at normal and
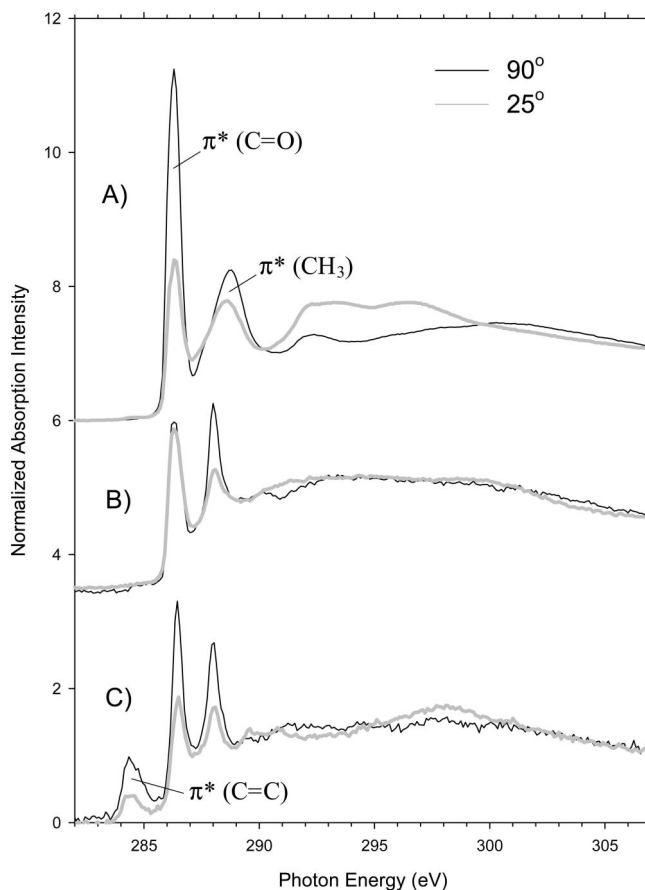

Figure 4. C k-edge NEXAFS spectra recorded at normal (black lines) and grazing (gray lines) angles of incidence. (A) Multilayer acetone produced by exposing $CeO_2(111)$ to 60 L of acetone at 95 K. (B) Oxidized $CeO_2(111)$ exposed to 5 L of acetone at 95 K followed by annealing at 175 K. (C) Reduced $CeO_{1.75}(111)$ exposed to 8 L of acetone at 150 K followed by annealing at 300 K.

grazing angles of incidence, indicating the molecular plane is tilted away from the surface normal. The $\pi*$ (CH$_3$) appears to have shifted to 288.2 eV. This feature may also have a contribution from the $\pi*$ (C=O) resonance from X-ray induced acetate that was observed in the C 1s spectra.[19] This feature has a strong absorption cross section so that only a small amount may produce significant intensity in the $\pi*$ resonance.

3.2. Acetone Reaction with Reduced CeO$_{2-x}$(111). The TPD following acetone adsorption on reduced $CeO_{1.75}(111)$ is shown by the gray curves in Figure 1. In addition to acetone (mass 43), the primary additional desorption products were H_2 (mass 2) and CO (mass 28). Acetone has a stronger desorption at higher temperatures from the reduced surface compared to the oxidized surface (black lines). A primary peak appears at 500 K with a weaker shoulder at ca. 560 K. The lower temperature peaks at 210 and 300 K on the oxidized surface are largely absent on the reduced surface. In subsequent TPDs, recorded by repeated cycles of re-exposing the surface to acetone at 140 K and heating to 900 K, the acetone desorption decreases in intensity, but the peak position and shape are essentially unchanged. The desorption from the fifth such cycle is indicated by the dotted lines in Figure 1.

H_2 desorbs in an intense doublet in the same temperature range as the acetone with a pair of peaks at ca. 500 and 580 K. There is also a small shoulder at 400 K and an even weaker signal above 800 K. This latter signal is nearly identical on the oxidized and reduced surfaces and may result from the sample holder or the mounting wires. In subsequent TPDs (dotted line),
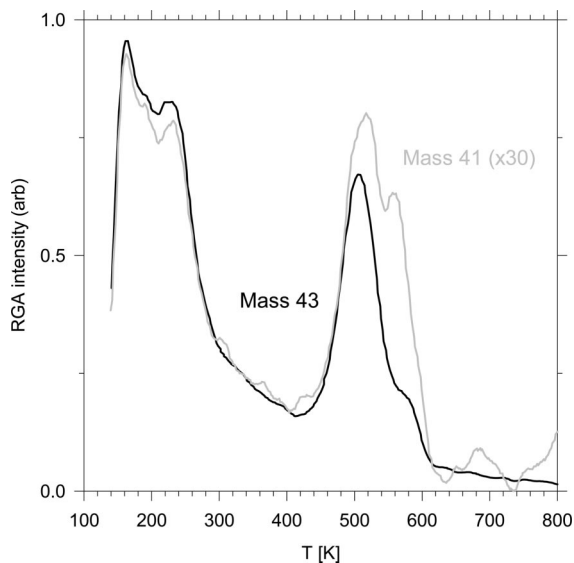
Acetone over CeO$_x$(111) Thin Films

J. Phys. Chem. C, Vol. 113, No. 15, 2009 **6211**

Figure 5. TPD of mass 43 (black) and mass 41 (gray) following adsorption of acetone on reduced CeO$_{1.75}$(111) at 140 K. Mass 41 has been magnified by a factor of 30 so that the signal near 200 K matches mass 43 to account for the acetone fragment at mass 41.
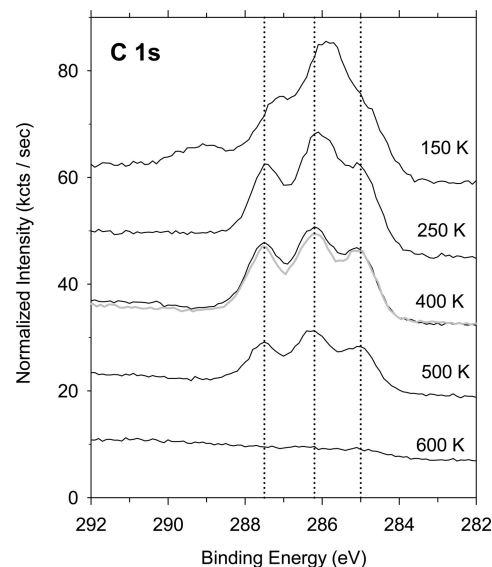

Figure 6. C 1s sXPS spectra following adsorption of acetone on reduced CeO$_{1.75}$(111) at 150 K and then annealed as indicated. The gray line was recorded in a separate experiment in which the acetone was adsorbed at 150 K and then immediately annealed to 400 K without exposing the surface to X-rays at lower temperatures.

the shoulder at 400 K disappeared and the peaks at 500 and 580 K increased in intensity but their relative intensities remained the same and their positions did not shift.

CO desorbs in a broad peak between 600 and 800 K. In subsequent TPDs, the peak shifted to higher temperatures so that after the fifth exposure the desorption occurred between 700 and 900 K and may not have been completed by 900 K (dotted line). The CO desorption lies on an increasing background that is probably related to desorption from the sample holder.

Masses 15, 18, 29, 31, 41, 42, 44, and 45 were monitored as markers for other possible products such as formaldehyde, methanol, ethanol, acetaldehyde, acetic acid, propylene, and 2,3-dimethyl-2-butene. The intensity at these masses near 200 K was scaled to match the intensity at mass 43 to account for the contribution from cracking fragments of acetone. Mass 41 was the only mass that showed any qualitative difference compared to mass 43, as plotted in Figure 5. Whereas mass 43 has a sharp peak at 500 K and a shoulder at 560 K, mass 41 has a clear peak at 560 K. Based on the absence of a definitive response from any product other than acetone at the other masses recorded, the additional product at 560 K is most likely propylene. However, the possibility that this is a coupling product such as 2,3-dimethyl-2-butene or 2,3-dimethyl-1,3-butadiene cannot be eliminated.[9] Note that this product has an intensity that is less than 3% of the acetone desorption intensity.

The C 1s sXPS spectrum following a 10 L exposure of acetone onto the clean surface of CeO$_{1.75}$(111) at 150 K is shown at the top of Figure 6. As on the CeO$_2$(111) surface, a small amount of weakly adsorbed acetone, with binding energies similar to multilayer acetone, is evident at 286 and 289 eV. There are also pronounced shoulders at 284.8 and 287.3 eV. Upon heating to 250 K, the weakly bound acetone desorbs leaving three remaining peaks at 285.0, 286.2, and 287.6 eV. The C 1s intensity decreases as the sample is annealed to 500 K, but the peak positions and relative intensities of these peaks do not vary significantly. These peaks can be tentatively assigned based on previously studied molecules. The binding energies of methoxy, dioxymethylene and formate were in the ranges of 287.2−287.9,[3] 288.2−289.0,[4] and 289−290 eV,[5] respectively.

On oxidized ceria, the peaks were located near the lower end of these binding energy ranges and shifted toward the higher ends on reduced surfaces. Further, the C 1s binding energies for methyl groups were observed at 286.0−286.9 eV for ethoxy and 2-propoxy (unpublished data). Therefore, the peaks at 286.2 and 287.6 eV appear to be related to methyl and alkoxy species, respectively. The peak at 285.0 eV is likely associated with a partially dehydrogenated alkyl species and will be discussed further below.

There was no C−C bond cleavage as indicated by the absence of an acetate feature at 290 eV. The absence of X-ray damage is also evident in the similarity of the black and gray spectra recorded at 400 K in Figure 6. As on the oxidized surface (Figure 2), the gray spectrum was recorded after adsorbing acetone at 95 K and then annealing the sample to the higher temperature without exposing the surface to X-rays at lower temperatures. The gray and black spectra at 400 K are virtually identical. The absence of X-ray induced bond cleavage is consistent with what was previously seen with formaldehyde where X-ray damage occurred on oxidized ceria but not on reduced ceria.[4] The C k-edge NEXAFS spectra from acetone adsorbed at 90 K on CeO$_{1.75}$(111) and then annealed to 300 K are shown in Figure 4c. The π* (C=O) resonance is evident at 286.5 eV. There is also a sharp resonance at 288 eV. Since there is no evidence of a carbonate-like species in the C 1s XPS (Figure 6), this feature is likely due to a π* (CH$_3$) resonance. The most interesting new feature is a peak at 284.5 eV. A peak in this position is generally associated with a π* (C=C) resonance.[20] The relative intensities of these three resonances are strongest at normal incidence indicating that the molecular plane is inclined toward the surface normal.

On the basis of the C 1s XPS and C k-edge NEXAFS, we can conclude that the chemisorbed intermediate has three unique types of C and contains C=O and C=C bonds. A model for a possible adsorption state is the carbanion shown in (3).

A possible configuration for bonding this carbanion to the surface is depicted in (4). This model is derived from the C 1s peak positions in Figure 6. In this configuration, the methyl carbon does not interact with the surface and has a binding

energy (286.2 eV) similar to those in acetone on oxidized ceria and to ethanol and 2-propanol. The central carbon has a binding energy of 287.6, in the range expected for an alkoxy. The remaining carbon is the deprotonated methyl group with binding energy of 285.0 eV and likely bonds to a surface Ce cation rather than an O anion since the Ce cation would cause an initial state chemical shift to a binding energy that is lower than the methyl C. Its binding energy is greater than would be observed for a carbide, however.[21]
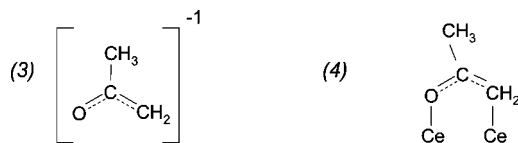
Heating to 600 K removes essentially all of the C 1s XPS signal. This is not consistent with the TPD which shows that CO desorption does not start until 600 K. The C must therefore be absorbed into the bulk of the ceria film, and the C 1s signal is totally attenuated due to the short electron mean free path at ca. 105 eV kinetic energy.

3.3. Reduction of Ceria by Acetone. Adsorption of acetone at 140 K followed by heating to elevated temperatures indicated little or no chemical interaction between acetone and $CeO_2(111)$. However, adsorption and reaction of acetone on partially reduced $CeO_{2-x}(111)$ produced H_2 and CO. Ce 3d XPS taken before and after the TPD indicated that the Ce was more reduced after the reaction. Experiments were conducted to determine if acetone will react with isolated defect sites on an oxidized surface at elevated temperatures.

Fully oxidized $Ce^{18}O_2(111)$ was exposed to ^{16}O-labeled acetone from a directed doser.[14] The sample temperature was maintained at 600 K. The exposure was started ten seconds after the RGA scan started and was allowed to run for 180 s. The only products detected were H_2 (mass 2), $C^{16}O$ (mass 28), $C^{18}O$ (mass 30), and acetone. In particular, no water or CO_2 were detected. Oxygen exchange occurred between the acetone and the surface as indicated by the detection of both labeled (mass 45) and unlabeled (mass 43) acetone. Mass 45 had ca. 20% of the intensity of mass 43. The response was recorded with the $CeO_2(111)$ surface facing toward the gas doser and with the sample rotated away from acetone reactant.

The evolution of H_2, labeled and unlabeled CO, and acetone during the exposure at 600 K is shown in Figure 7. One of the striking features is a significant lag between the start of the exposure at ten seconds and the peak of product formation at ca. 55 s. As shown in the TPD experiments (Figure 1), CO and H_2 are only produced from a reduced surface. The small amount of CO and H_2 suggests that the acetone is reacting at a small number of reduced ceria sites such as O defect sites or edge sites. Initially, there are relatively few of these types of sites on the surface and the reaction is slow. As the reaction proceeds CO is produced creating more vacancies and the reaction accelerates. The acetone signal is inversely related to the H_2 and CO signals. As the H_2 and CO signals increase, the acetone intensity decreases.

The mass 30 signal is initially much stronger than the mass 28 signal. This indicates that the C in the methyl groups is reacting with the ^{18}O in the $Ce^{18}O_2$ substrate. The mass 30 signal decays more than the mass 28 signal. The decay of $C^{18}O$ indicates that it becomes more difficult for C in the methyl groups to react with the O in the ceria. However, CO formed
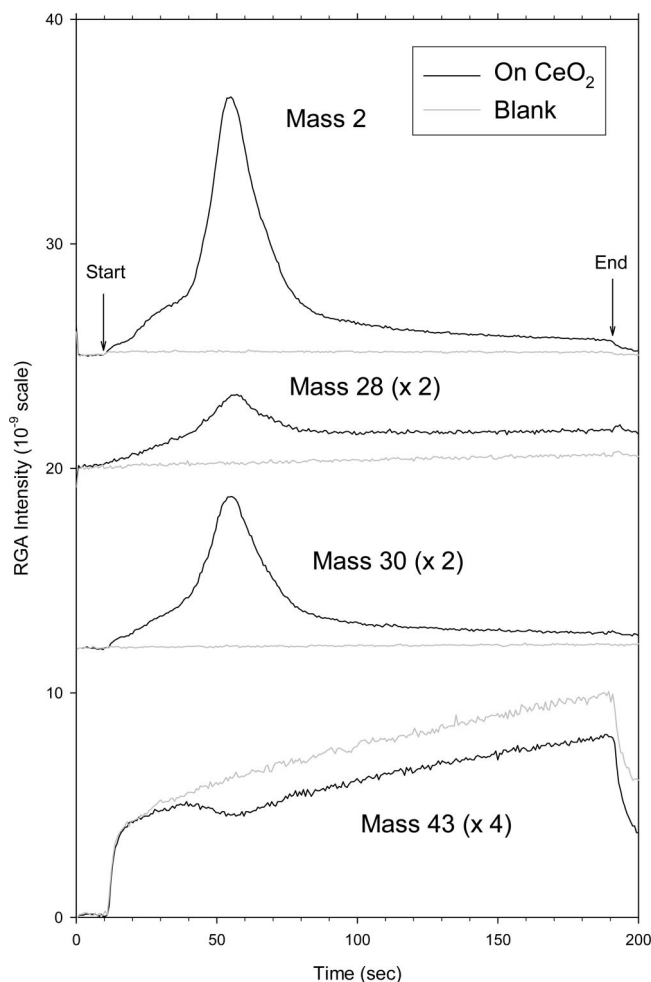

Figure 7. Reaction profiles recorded during the exposure of $Ce^{18}O_2(111)$ to ^{16}O-labeled acetone at 600 K. The acetone flux was ca. 1×10^{14} molecules cm^{-2} s^{-1}. The gray lines indicate the response when the sample is moved away from the doser.

from the carbonyl part of the acetone continues to be produced as indicated by the larger $C^{16}O$ signal.

After the acetone exposure at 600 K the sample was annealed to 900 K to remove residual C. Ce 3d XPS indicated that the ceria was reduced to 30% Ce^{4+}. The surface was then re-exposed to acetone at 600 K and the reaction profile is shown in Figure 8. H_2 is produced instantaneously. There is very little CO produced and the unlabeled $C^{16}O$ is slightly more intense than the labeled $C^{18}O$. These results suggest that acetone can react and decompose on the reduced surface but then the decomposition fragments are unable to react with surface O thus poisoning further reaction.

C 1s and O 1s sXPS spectra following exposure of oxidized $CeO_2(111)$ to 90 L of acetone at 600 K are shown in Figure 9. Only a single peak is evident in the C 1s spectrum; however, it is broader than the C 1s peaks shown in Figure 3. The spectrum consists primarily of a peak at 285 eV that was assigned to CH_2 bonded to Ce in Figure 6. The added breadth may be due to longer chain alkyl fragments, i.e., C bonded to C rather than to the surface. The O 1s spectrum following acetone exposure at 600 K (Figure 9b, black line) shows only a single peak at 530.1 eV. This is in the same position as the peak for the lattice O on the clean surface (gray line). This demonstrates that the C is not bonded to surface O, since we have previously shown that the O 1s peaks associated with hydroxyl, methoxy, formate, and carbonate on $CeO_{2-x}(111)$ are shifted away from the lattice O peak and lie between 532 and 534 eV.[3,5,22]
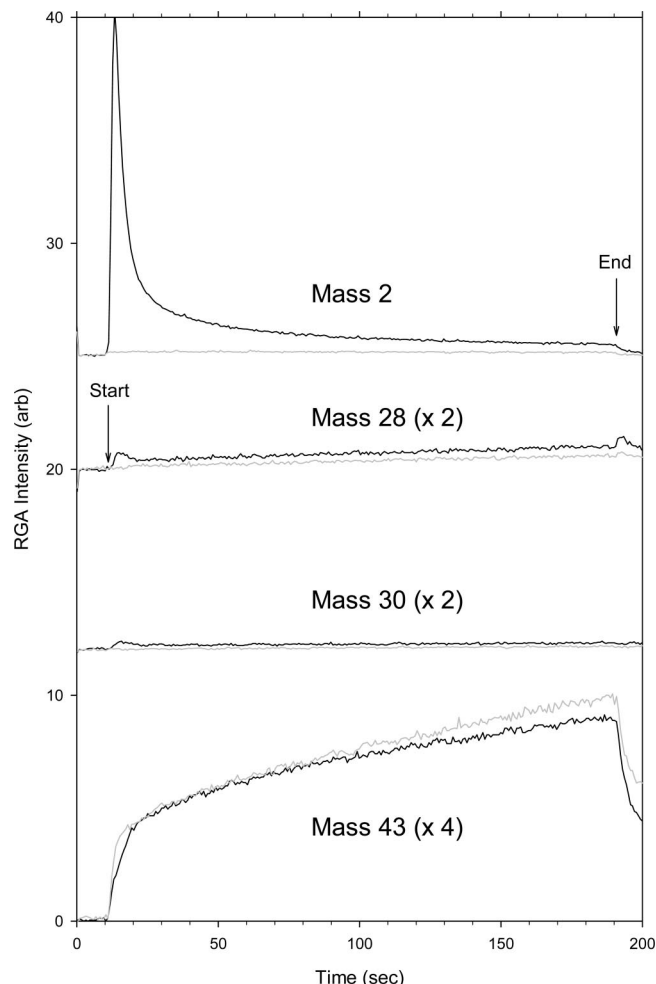
Acetone over CeO_x(111) Thin Films

J. Phys. Chem. C, Vol. 113, No. 15, 2009 **6213**

Figure 8. Reaction profiles recorded during a second exposure of $Ce^{18}O_2(111)$ to ^{16}O-labeled acetone at 600 K. Between the first exposure shown in Figure 8 and the exposure shown above, the sample was annealed to 900 K. The acetone flux was ca. 1×10^{14} molecules cm^{-2} s^{-1}. The gray lines indicate the response when the sample is moved away from the doser.

4. Discussion

Acetone adsorbs on the $CeO_2(111)$ surface at low temperatures without breaking the central carbonyl bond (C=O). This is evident from the NEXAFS spectrum where the π^*(C=O) feature is evident in the chemisorbed species. The surface species is therefore assigned to η_1-acetone (1) rather than to dioxypropylene (2). This is in contrast to the case of formaldehyde on $CeO_2(111)$ where NEXAFS data pointed to the loss of π^*(C=O) in the formation of the dioxymethylene intermediate.[4]

When reduced $CeO_{2-x}(111)$ is exposed to acetone at low temperatures the adsorption and reaction behavior is considerably different. From the TPD (Figure 1, gray lines) it can be seen that the acetone is more strongly bound than on $CeO_2(111)$, and some of the acetone undergoes total decomposition to CO and H_2. Since this adsorption and reaction behavior occurs on the reduced surface but not on an oxidized surface, surface O-vacancies are apparently necessary. The C 1s core level spectra indicate that at least three types of C are present in the chemisorbed species. The three C 1s peaks have roughly equal intensity suggesting that they are associated with the three C atoms present in the acetone adsorbate. Further, the overall C 1s intensity decreases between 400 and 500 K, but the relative intensities of the three peaks remain the same indicating that
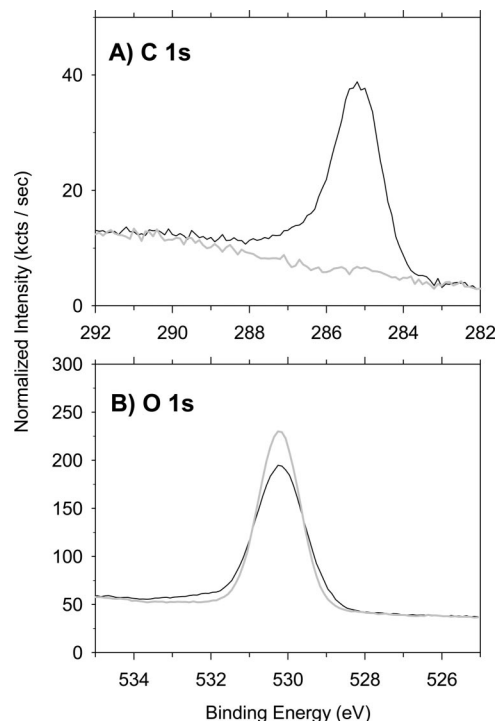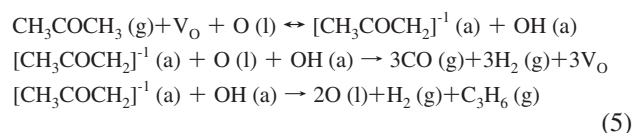

Figure 9. (A) C 1s and (B) O 1s sXPS spectra recorded following the exposure of $CeO_2(111)$ to acetone at 600 K (black). The gray lines were recorded from a clean, reduced $CeO_{1.75}(111)$ surface.

the same species leads to acetone desorption below 500 K and H_2 and CO desorption above 500 K. The NEXAFS spectra indicate the presence of both π^* (C=O) and π^* (C=C) resonances. The C 1s and NEXAFS data support the identification of a carbanion intermediate (3). The C 1s peak positions further suggest that the carbanion is bound to the Ce cations. This is consistent with the necessity of having O-vacancies which expose Ce cations. The overall behavior on the reduced surface can be summarized as (5)

$$CH_3COCH_3 (g) + V_O + O (l) \leftrightarrow [CH_3COCH_2]^{-1} (a) + OH (a)$$
$$[CH_3COCH_2]^{-1} (a) + O (l) + OH (a) \rightarrow 3CO (g) + 3H_2 (g) + 3V_O$$
$$[CH_3COCH_2]^{-1} (a) + OH (a) \rightarrow 2O (l) + H_2 (g) + C_3H_6 (g)$$

$$(5)$$

where O (l) is lattice O and V_O is an O vacancy site.

The reversible desorption of acetone from the recombination of the carbanion and surface hydroxyl is limited by reaction of hydroxyls to produce H_2 which occurs at the same temperature.[22] When the hydroxyl is depleted the carbanion becomes trapped on the surface until it decomposes into CO and H_2. Note that the third pathway, which would lead to ceria oxidation, is a very minor contribution as shown in Figure 5.

The carbanion proposed in this work (3), and the C 1s XPS data that supports the assignment (Figure 6), are similar to what was proposed by Gutierrez-Sosa et al. for acetone on ZnO(0001)−Zn.[23] The C 1s peak positions and relative intensities observed in Figure 6 are nearly identical to those obtained from acetone on ZnO(0001)−Zn. However, the NEXAFS recorded from acetone on these two surfaces lead to slightly different conclusions. The π^* (C=O) resonance is evident in the NEXAFS spectra from both surfaces however the π^* (C=C) resonance is only seen on reduced $CeO_{2-x}(111)$. This suggests that on $CeO_{2-x}(111)$ the double bond is delocalized across the

O−C−C atoms whereas on ZnO(0001)−Zn the double bond is localized between the C−O.

When CeO$_2$(111) is exposed to acetone at elevated temperatures (600 K), the acetone reacts with surface O yielding CO and H$_2$ and leading to a net reduction of the ceria as follows (6):

$$CH_3COCH_3 \text{ (g)} + 2O \text{ (l)} \rightarrow 3CO \text{ (g)} + 3H_2 \text{ (g)} + 2V_O \quad (6)$$

$$CH_3COCH_3 \text{ (g)} + 2 V_O \rightarrow 2CH_x \text{ (a)} + CO \text{ (g)} + H_2 \text{ (g)} \quad (7)$$

where O(*l*) is lattice O and V$_O$ is an O vacancy site. Reaction *(6)* occurs on a predominantly oxidized surface (Figure 7) and leads to ceria reduction. Reaction (7) occurs on a predominantly reduced surface (Figure 8). The nature of the adsorbed CH$_X$ is not entirely known but the C 1s and O 1s spectra (Figure 9) indicate that they are adsorbed at Ce cation sites.

The reaction profiles shown in Figures 7 and 8, as well as the behavior on reduced ceria, suggest that the acetone requires O vacancy/defect sites to react with the surface.

5. Summary

- Acetone weakly chemisorbs on oxidized CeO$_2$(111) in an η_1 configuration.
- Acetone binds strongly as a carbanion on reduced CeO$_{2-x}$(111).
- The carbanion can recombine with surface hydroxyl to desorb as acetone at 500 K or can react with surface O to decompose into CO and H$_2$.
- At 600 K acetone can adsorb at O-defect sites and react with surface O resulting in extensively reduced ceria.

References and Notes

(1) *Catalysis by Ceria and Related Materials*; Trovarelli, A., Ed.; Imperial College Press: London, 2002.
(2) Mullins, D. R.; Overbury, S. H.; Huntley, D. R. *Surf. Sci.* **1998**, *409*, 307.
(3) Mullins, D. R.; Robbins, M. D.; Zhou, J. *Surf. Sci.* **2006**, *600*, 1547.
(4) Zhou, J.; Mullins, D. R. *Surf. Sci.* **2006**, *600*, 1540.
(5) Senanayake, S. D.; Mullins, D. R. *J. Phys. Chem. C* **2008**, *112*, 9744.
(6) Overbury, S. H.; Mullins, D. R.; Huntley, D. R.; Kundakovic, L. *J. Catal.* **1999**, *186*, 296.
(7) Vohs, J. M.; Barteau, M. A. *J. Phys. Chem.* **1991**, *95*, 297.
(8) Henderson, M. A. *J. Phys. Chem. B* **2004**, *108*, 18932.
(9) Pierce, K. G.; Barteau, M. A. *J. Org. Chem.* **1995**, *60*, 2405.
(10) King, R. I.; Senanayake, S. D.; Chong, S. V.; Idriss, H. *Surf. Sci.* **2007**, *601*, 5690.
(11) Henderson, M. A. *J. Phys. Chem. B* **2005**, *109*, 12062.
(12) Mullins, D. R.; Radulovic, P. V.; Overbury, S. H. *Surf. Sci.* **1999**, *429*, 186.
(13) Zhou, J.; Baddorf, A. P.; Mullins, D. R.; Overbury, S. H. *J. Phys. Chem. C* **2008**, *112*, 9336.
(14) Hagans, P. L.; Dekoven, B. M.; Womack, J. L. *J. Vac. Sci. Technol. A* **1989**, *7*, 3375.
(15) Liu, J.; Xu, M.; Nordmeyer, T.; Zaera, F. *J. Phys. Chem.* **1995**, *99*, 6167.
(16) Armstrong, J. L.; White, J. M.; Langell, M. *J. Vac. Sci. Technol. A* **1997**, *15*, 1146.
(17) Adams, D. L. *FitXPS 2.12*, 2001.
(18) Sekiguchi, T.; Ikeura-Sekiguchi, H.; Baba, Y. *Surf. Sci.* **2000**, *454*, 363.
(19) Lee, H. K.; Kim, K. J.; Han, J. H.; Kang, T. H.; Chung, J. W.; Kim, B. *Phys. Rev. B* **2008**, *77*.
(20) Stohr, J. NEXAFS Spectroscopy; Springer-Verlag: New York, 2003; p 25.
(21) Ramqvist, L. *J. Appl. Phys.* **1971**, *42*, 2113.
(22) Kundakovic, L.; Mullins, D. R.; Overbury, S. H. *Surf. Sci.* **2000**, *457*, 51.
(23) Gutierrez-Sosa, A.; Evans, T. M.; Parker, S. C.; Campbell, C. T.; Thornton, G. *Surf. Sci.* **2002**, *497*, 239.

JP810403D