ABSTRACT: Adsorption and decomposition of acetic acid were studied by means of synchrotron radiation photoelectron spectroscopy, resonant photoemission spectroscopy, and temperature-programmed desorption on Pt/CeO$_2$(111) model catalysts prepared on Cu(111). Reference experiments under identical conditions were performed on stoichiometric CeO$_2$(111), partially reduced CeO$_{2-x}$, and oxygen pre-exposed O/Pt/CeO$_2$(111)/Cu(111). The principal species formed on all samples during adsorption of acetic acid at 150 K were acetate and molecularly adsorbed acetic acid. On the basis of the differences in the splitting between the methyl and carboxyl/carboxylate groups in the C 1s spectra, we identified the adsorption sites for acetate and molecularly adsorbed acetic acid on Pt/CeO$_2$. During annealing, we detected an increase in the concentration of acetate on CeO$_2$(111) support exclusively in the presence of supported Pt particles. The effect is caused by the decomposition of molecularly adsorbed acetic acid on Pt particles followed by spillover of acetate to CeO$_2$(111) support. The following surface crowding by acetate on CeO$_2$(111) support alters the decomposition mechanism of acetate with respect to the Pt-free CeO$_2$(111). In particular, the formation of ketene and acetone was largely eliminated on Pt/CeO$_2$. We assume that the surface crowding by acetate triggers a switch in the adsorption geometry of acetate from the bidentate to the monodentate configuration. The acetates in both adsorption geometries were identified according to the differences in the splitting between the methyl and carboxylate groups in the C 1s spectra. Decomposition of acetate did not leave behind any surface carbon on Pt-free CeO$_2$. In contrast, carbonaceous residues were found on CeO$_{2-x}$ and Pt/CeO$_2$. The carbon residues were oxidatively removed above 500 K only from Pt/CeO$_2$.

1. INTRODUCTION

Hydrogen production from biomass-derived oxygenates has recently received considerable attention.$^{1,2}$ From such feedstocks, steam reforming is among the most efficient technologies for large-scale hydrogen production. The reaction has recently been studied on numerous catalyst materials including various supported Pt catalysts, often on reducible oxide supports such as ceria.$^{2-6}$ Carboxylic acids, for example, acetic acid (CH$_3$COOH), are an abundant component in the biomass-derived feedstock.$^7$ Moreover, acetic acid represents an ideal model component for fundamental studies of reforming mechanisms, as the molecule contains C–H, C–O, and C–C bonds. A better understanding of the activation mechanisms of the different bonds is also relevant for other applications. For example, Pt–CeO$_2$ has been proposed as a fuel cell catalyst.$^8$

Here, hydrocarbon oxygenates may be used as fuels but may also play a role as side products and intermediates leading to poisoning and degradation phenomena.

In previous studies, complex reaction patterns have been found that involve the formation of undesirable side products such as acetone.$^9$ It was argued that oligomerization of acetone causes formation of coke and, therefore, catalyst deactivation. Notably, the formation of acetone was found to be significantly suppressed on Pt/CeO$_2$. Due to the complexity of powder catalysts, however, the microscopic origins of the underlying surface reaction mechanism remained largely unexplored.
More detailed insights into the underlying reaction mechanisms are available from the model studies on single crystal surfaces and on single-crystal-based model catalysts.10−13 Using a surface science approach, the adsorption and reaction of acetic acid has been studied both on metallic14−26 and oxide27−36 surfaces. To the best of our knowledge, no studies have been performed on supported model catalysts so far (i.e., on metal nanoparticles on well-defined oxide surfaces). Earlier, the model approach enabled the identification of the active sites and allowed the monitoring of the surface species spillover during the decomposition of formic acid on Pt/CeO2(111)/Cu(111).37

On many metal and oxide surfaces, partial depnoration of acetic acid occurs above 150 K, leading to the formation of acetate. On noble metals, acetate predominantly recombines with hydrogen and desorbs upon heating. However, a significant fraction may also undergo decomposition to CO, CO2, hydrogen, and water.17−20 More complex decomposition patterns have been reported on oxide surfaces, such as CeO2 and TiO2. On these surfaces, ketene and water were proposed as the major products of acetate dehydration.33−35 Additionally, byproducts such as aceton, acetadehyde, hydrogen, and acetylene have been reported.31−34 The amount of these byproducts depends both on the surface stoichiometry and on the structure of the oxide.32,33 In particular, it was found that acetone is the product of a bimolecular ketonization that occurs upon coordination of two acetates to one common metal cation.35,36 Although the formation of acetone has been reported on real ceria-based catalysts,38 where it has been related to coke formation, its contribution to coke formation is less clear from surface science studies. Senanayake et al.39 reported that acetone reacts strongly with partially reduced CeO2−x only. However, the decomposition of acetone-derived species occurred below 600 K without any carbonaceous deposits left on the surface.

On the basis of the above-mentioned work on pure metal and oxide surfaces, we address, in this work, the reaction mechanism of acetic acid on Pt/CeO2(111) supported model catalysts. The principal challenge lies in the complexity of the surface, giving rise to numerous species and reaction pathways. In order to identify the individual species, we performed reference experiments under identical conditions on stoichiometric CeO2(111) and partially reduced CeO2−x(111). Concerning the role of Pt, we refer to our recent study14 of acetic acid decomposition on clean Pt(111) and oxygen precoverted, p(2 × 2)−O/Pt(111). The analysis of the adsorbed species on these simpler surfaces allows us to identify intermediates and new reaction channels on complex supported model catalysts in the present study.

2. MATERIALS AND METHODS

2.1. Sample Preparation. A single crystal Cu(111) disc (MaTecK GmbH, 99.999%) was used as a substrate for the preparation of the CeO2(111) and CeO2−x films. Cu(111) was cleaned by several cycles of Ar+ sputtering (300 K, 60 min) and annealing (723 K, 5 min) until no traces of carbon or any other contaminant were found in the photoelectron spectra. Epitaxial CeO2(111) films were prepared by Physical Vapor Deposition (PVD) of Ce metal (Goodfellow, 99.99%) from an electron beam evaporator (Tectra e-flux) in an oxygen atmosphere (pO2 = 5 × 10−7 mbar, Linde, 99.999%) at 523 K, followed by annealing of the films at 523 K in an oxygen atmosphere at the same pressure for 5 min. The prepared CeO2(111) films were characterized in situ by means of X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED). It was found that the preparation method40 yielded a continuous,34 stoichiometric CeO2(111) film with a thickness in the range of 1.9−2.1 nm (i.e., ~6−7 O−Ce−O monolayers), as determined from the attenuation of the Cu 2p3/2 intensity. The LEED confirmed the epitaxial growth of CeO2(111) with the characteristic (1.5 × 1.5) superstructure relative to the Cu(111) substrate in line with earlier studies.40,42 According to previous scanning tunneling microscopy (STM) studies, flat CeO2(111) terraces are separated by steps showing defect structures similar to those on single crystal CeO2(111) and contain extended rough patches.43,44 The height profile of the CeO2 film shows that 3−4 monolayers are open. The estimated coverage of the step edge atoms is about 11%.44

The partially reduced ceria film (CeO2−x) was prepared by exposing a stoichiometric CeO2(111) film to 70 L of methanol by backfilling the chamber (5 × 10−8 mbar, 30 min) at a sample temperature of 700 K, followed by annealing in ultrahigh vacuum (UHV) for 30 min. The procedure yields CeO2−x films, where x = 0.2.

Pt (Goodfellow, 99.99%) was deposited by PVD from an electron beam evaporator (Oxford Scientific OS-Vap) onto the CeO2(111)/Cu(111) at 300 K. The nominal thickness of the deposited Pt layer was 0.4 nm, equivalent to 1.7 ML, as determined from the attenuation of the Cu 2p3/2 intensity. This procedure yielded three-dimensional Pt particles with the corresponding average diameter of 3.4 ± 0.6 nm, mean height of 1.1 ± 0.4 nm, and the particles density on the CeO2(111) surface of (9.1 ± 0.9) × 1012 cm−2.45 The Pt/CeO2/Cu(111) sample was briefly heated to 500 K prior to acetic acid adsorption in order to remove potential surface impurities (such as CO) accumulated during the sample preparation. According to our previous studies,46 annealing of Pt/CeO2/Cu(111) to 500 K causes mild sintering of Pt particles that has rather minor effect on the Pt coverage. At a temperature up to 700 K, moderate morphological changes occur that involve coalescence and Ostwald ripening of Pt particles.46 Additionally, oxygen reverse spillover is triggered above 500 K.37

The binding energy of Pt 4f core level obtained from as-prepared Pt/CeO2/Cu(111) is 71.06 eV, consistent with formation of metallic Pt particles. Annealing to 500 K resulted in a shift of the binding energy to 71.03 eV. The O/Pt/CeO2/Cu(111) model catalyst was prepared as follows: First Pt/CeO2/Cu(111) was briefly heated to 500 K, then it was exposed to 20 L of O2 at 200 K, followed by a flash to 500 K. This procedure resulted in reoxidation of Ce3+ centers formed during Pt deposition (data not shown). Finally, the sample was exposed to 50 L of O2 at 200 K again followed by a flash to 220 K. This procedure caused a shift of Pt 4f core level to 71.10 eV. The corresponding shift is consistent with chemisorption of oxygen on Pt particles.48

Acetic acid (Sigma-Aldrich, 99.98%) was purified by several freeze−pump−thaw cycles. The investigated samples were exposed in consecutive doses to a total amount of 15 L of acetic acid at 150 K by backfilling the UHV chamber.

2.2. Temperature-Programmed Desorption (TPD). The temperature-programmed desorption (TPD) experiments were performed in a UHV system (base pressure 1 × 10−10 mbar) at the Charles University in Prague, Czech Republic. The chamber was equipped with a quadruple mass spectrometer (QMS, Pfeiffer PrismaPlus), which was placed behind a differentially pumped nozzle in order to separate background contributions.
from molecules desorbing directly from the sample surface. The samples were heated resistively and were attached to a liquid-nitrogen-cooled cryostat, enabling us to reach sample temperatures between 90 and 1200 K. The temperature was ramped at a rate of 2 K/s.

2.3. Synchrotron Radiation Photoelectron Spectroscopy (SRPES) and Resonant Photoemission Spectroscopy (RPES). High-resolution synchrotron radiation photoelectron spectroscopy (SRPES) and resonant photoemission spectroscopy (RPES) studies were performed at the Materials Science Beamline (MSB), Elettra synchrotron light facility in Trieste, Italy. The MSB, with a bending magnet source, provides synchrotron light in the energy range of 21−1000 eV. The UHV end-station (base-pressure 1 × 10^{-10} mbar) was equipped with a multichannel electron energy analyzer (Specs Phoibos 150), a rear view LEED optics, an argon sputter gun, and a gas inlet system. The basic setup of the chamber includes a dual Mg/Al X-ray source. Additionally, two electron-beam evaporators for Ce and Pt deposition were installed. Core level spectra of O 1s and C 1s were acquired at 650 and 410 eV, respectively. The binding energies in the spectra acquired with synchrotron radiation were calibrated with respect to the Fermi level. Additionally, Al Kα radiation (1486.6 eV) was used to measure O 1s, C 1s, Ce 3d, and Cu 2p3/2 core levels. All spectra were acquired at constant pass energy and at an emission angle for the photoelectrons of 20° or 0° with respect to the sample normal, while using the X-ray source or synchrotron radiation, respectively.

Valence band spectra were acquired at three different photon energies, 121.4, 124.8, and 115.0 eV, which correspond to the resonant enhancements in Ce^{3+}, Ce^{4+} ions, and to off-resonance conditions, respectively. Analysis of the spectra obtained with these photon energies forms the basis of RPES.57,49 The Ce^{3+} resonance at a photon energy of 121.4 eV is caused by a super Coster–Kronig decay involving electron emission from Ce 4f states located about 1.4 eV below the Fermi edge. The Ce^{4+} resonance at a photon energy of 124.8 eV involves emission of O 2p electrons (hybridized with Ce states) from the valence band around 4.0 eV. The valence band spectrum measured at a photon energy of 115 eV is used as a background for the
calculation of the intensity difference of the features on- and off-resonance, denoted as the resonant enhancements for Ce\(^{3+}\) \((D(\text{Ce}^{3+}))\) and for Ce\(^{4+}\) \((D(\text{Ce}^{4+}))\), respectively. The resonant enhancement ratio (RER), calculated as \(D(\text{Ce}^{3+})/D(\text{Ce}^{4+})\), is the direct measure of the degree of reduction of the cerium oxide.

The values of total spectral resolution were 1 eV (Al K\(\alpha\)), 200 meV \((h\nu = 115–180 \text{ eV})\), 400 meV \((h\nu = 410 \text{ eV})\), and 650 meV \((h\nu = 650 \text{ eV})\). The C 1s core level spectra were fitted with a Voigt profile after subtraction of a Shirley background.

All SRPES and RPES data were processed using KolXPD fitting software.\(^{50}\)

During the experiment, the sample temperature was controlled by a DC power supply passing a current through Ta wires holding the sample. Temperatures were monitored by a K-type thermocouple attached to the back of the sample. Stable temperature and fast cooling were achieved by simultaneous resistive heating of the sample and cooling of the manipulator with liquid nitrogen.

Figure 2. Integrated intensities of C 1s spectral components (a, b, d, e) and RER (c, f) as a function of exposure (a, d) and temperature (b, c, e, f) on CeO\(_2\)(111) (a–c) and CeO\(_2\)\(_{2-x}\) (d–f). The C 1s spectra were acquired with \(h\nu = 410 \text{ eV}\). For clarity, the \((2')\) component is not plotted in (a, b, d, e) as it is equal in intensity to (2).
3. RESULTS AND DISCUSSION

3.1. Adsorption and Decomposition of Acetic Acid on Stoichiometric CeO$_2$(111). Adsorption of acetic acid on the stoichiometric CeO$_2$(111)/Cu(111) film at 150 K yields acetate and molecular acetic acid. The corresponding C 1s spectra are shown in Figure 1a. Two peaks at 285.3 (1) and 288.7 eV (1') arise from methyl (−CH$_3$) and carboxylate (−COO$^-$) groups in the acetate (CH$_3$COO$^-$) species, respectively. At higher exposures, these are accompanied by the peaks at 286.0 (2) and 289.6 eV (2') arising from methyl and carboxyl (−COOH) groups in molecularly adsorbed acetic acid. The average splittings between the methyl and carboxyl/carboxylate groups in acetate and acetic acid are 3.4 and 3.6 ± 0.1 eV, respectively. The observed splittings in acetate and acetic acid adsorbed on CeO$_2$ are smaller than the 4.0 eV splitting between the methyl and carboxyl carbons observed in gaseous acetic acid.31

The integrated C 1s intensities of the observed peaks are plotted in Figure 2a as a function of the acetic acid exposure. The intensities of the methyl (2) and carboxyl (2') groups in acetic acid are equal indicating a random orientation of adsorbed acetic acid molecules on CeO$_2$.

In contrast, the intensity of the methyl group (1) is higher than that of the corresponding carboxylate (1') group in acetate, as expected for a molecular orientation with the methyl group pointing toward the vacuum.

The development of the C 1s spectra during stepwise annealing of the stoichiometric CeO$_2$(111) exposed to 15 L of acetic acid at 150 K is shown in Figure 1a. The peaks associated with molecularly adsorbed acetic acid, (2) and (2'), decrease in intensity until they vanish at 250 K. The corresponding peaks (1) and (1') show a gradual shift to higher binding energies until they vanish at 550 K. During adsorption and annealing, the splittings between methyl and carboxyl/carboxylate groups in acetic acid and acetate do not vary significantly. The integrated C 1s intensities of the observed peaks are plotted in Figure 2b as functions of temperature. One can see that annealing initially results in a moderate increase of the (1') intensity, while the acetic acid signals are decreasing. In contrast, the intensity of peak (1) remains practically unchanged up to 450 K.

Analysis of the desorption spectra obtained from the stoichiometric CeO$_2$(111) film reveal partial decomposition of molecular acetic acid below 250 K. Selected TPD spectra are shown in Figure 3 (black lines). Desorption of molecular acetic acid at 193 K was identified by the presence of the m/z fragments at 43, 45, and 60. Desorption of acetic acid is rapidly followed by desorption of ketene (m/z = 14), acetaldehyde (m/z = 29, 43, 44), water (m/z = 18), CO (m/z = 28), and H$_2$ (m/z = 2) at 197 K. Analysis of the corresponding m/z ratios 14, 29, and 45 yielded 50% of ketene, 15% of acetaldehyde, and 35% of molecular acetic acid (gas specific sensitivity factors were not taken into account). Except for a small amount of water desorbing at about 300 K, no other products are formed on CeO$_2$(111) below 450 K. The major decomposition products of acetic acid on CeO$_2$(111) above 450 K are water, ketene, CO, and CO$_2$ (m/z = 44). Desorption of ketene occurs through two distinct channels at 506 and 589 K. Water, CO, and CO$_2$ accompany both channels, but the desorption maxima of these products are slightly shifted to higher temperature (609 K), suggesting an additional decomposition channel that does not involve ketene.

Numerous minor products form upon decomposition of acetate on CeO$_2$(111). We identified acetone (m/z = 43, 58), acetaldehyde, molecular acetic acid, ethylene (m/z = 26, 27), acetylene (m/z = 26), and H$_2$. All products are listed in Table 1. More detailed analysis of the desorption products and their distribution is given in the Supporting Information.

Decomposition of acetic acid on CeO$_2$(111)/Ru(0001) films has been studied previously by Mullins et al.33 The most significant difference between CeO$_2$(111)/Ru(0001) and CeO$_2$(111)/Cu(111) concerns the decomposition channel at 506 K. In contrast to the case of CeO$_2$(111)/Cu(111), this channel appears to be suppressed on CeO$_2$(111)/Ru(0001). We note that this decomposition channel becomes less pronounced in the second run of TPD also on CeO$_2$(111)/Cu(111) (see Supporting Information). This observation suggests that the difference between CeO$_2$(111) on Cu(111) and Ru(0001) could be related to the different degrees of reduction of as-prepared CeO$_2$(111) films. Additionally, we...
Table 1. Desorbing Products Observed during TPD from CeO$_2$(111)/Cu(111) and CeO$_{2-x}$/Cu(111) Following Exposure to 15 L of Acetic Acid at 150 K$^a$

<table>
<thead>
<tr>
<th>T [K]</th>
<th>193</th>
<th>197</th>
<th>300</th>
<th>506</th>
<th>583</th>
<th>589</th>
<th>595</th>
<th>609</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$(111)</td>
<td>CH$_3$COOH</td>
<td>CH$_3$OH</td>
<td>H$_2$O</td>
<td>CO</td>
<td>H$_2$</td>
<td>CO$_2$</td>
<td>CH$_3$CHO</td>
<td>(CH$_3$)$_2$CO</td>
<td>CO</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_5$OH</td>
<td>CH$_3$CO</td>
<td>H$_2$</td>
<td>CN</td>
<td>CH$_3$CO</td>
<td>CO$_2$</td>
<td>CH$_3$CHO</td>
<td>(CH$_3$)$_2$CO</td>
<td>H$_2$</td>
</tr>
<tr>
<td>CeO$_{2-x}$/Cu(111)</td>
<td>CH$_3$COOH</td>
<td>CH$_3$OH</td>
<td>H$_2$O</td>
<td>CO</td>
<td>H$_2$</td>
<td>CO$_2$</td>
<td>CH$_3$CHO</td>
<td>(CH$_3$)$_2$CO</td>
<td>CO</td>
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<tr>
<td></td>
<td>C$_2$H$_5$OH</td>
<td>CH$_3$CO</td>
<td>H$_2$</td>
<td>CN</td>
<td>CH$_3$CO</td>
<td>CO$_2$</td>
<td>CH$_3$CHO</td>
<td>(CH$_3$)$_2$CO</td>
<td>H$_2$</td>
</tr>
</tbody>
</table>

$^a$The products designated in bold represent majority species at each desorption temperature.

found that unlike the situation for CeO$_2$(111)/Ru(0001), acetylene is formed only above 650 K, while ethylene accompanies the production of ketene at 506 and 589 K on CeO$_2$(111)/Cu(111). Similar to CeO$_2$(111)/Cu(111), Mullins et al. also observed desorption of water at 300 K. The authors suggested that water results from the recombination of surface hydroxyl groups. Similarly, desorption of water has been observed during the decomposition of formic acid on CeO$_2$(111) films. The production of water at 300 K does not cause reduction of CeO$_2$(111)/Cu(111). The corresponding evolution of resonant enhancement ratio (RER) is plotted in Figure 2c as a function of temperature. We did not observe any significant change of the RER up to 500 K. Above 500 K, decomposition of acetate causes slight reduction of CeO$_2$(111) giving rise to a small number of Ce$^{3+}$ cations and associated oxygen vacancies. We assume that this hydrogen desorbing between 506 and 609 K reacts with lattice oxygen to form water.

3.2. Adsorption and Decomposition of Acetic Acid on Partially Reduced CeO$_{2-x}$/Films. C 1s spectra obtained from the partially reduced CeO$_{2-x}$/Cu(111) film exposed to increasing doses of acetic acid at 150 K are shown in Figure 1b. Similarly to CeO$_2$(111)/Cu(111) (see Section 3.1), we assign the peaks at 286.1 (1) and 290.0 (1$'$) to acetate and the peaks at 286.7 (2) and 290.4 eV (2$'$) to acetic acid, respectively. Note that the corresponding binding energies of acetate and acetic acid adsorbed on the partially reduced CeO$_{2-x}$/film are by about 1 eV higher with respect to the same species on stoichiometric CeO$_2$(111) surface (see Section 3.1). Similar shifts to higher binding energies for the species adsorbed on partially reduced ceria have been observed with numerous oxygenates. The average splittings between the methyl and carboxyl/carboxylate groups in acetic acid and acetate are 3.7 and 3.5 ± 0.1 eV, respectively. The peak at 287.2 eV (3) was not found on stoichiometric CeO$_2$(111). On the basis of the observed binding energy, we attribute this species to an alkoxo moiety (e.g., methoxy (CH$_3$O$^-$)). The integrated C 1s intensities of the observed peaks are plotted in Figure 2d as a function of acetic acid exposure. In the limit of low exposures, the intensity of the methyl group (1) is slightly lower than that of the carboxylate group (1$'$) in acetate on CeO$_{2-x}$. Additionally, we observed a shift of the corresponding peak (1$'$) from 290.0 to 289.5 eV with an increasing dose of acetic acid. It is possible that at exposures below 5 L, the peak (1$'$) contains a contribution from other surface species (e.g. formate or carbonate (CO$_3^{2-}$)). Considering the binding energies of carbonate (290.0 eV) and formate (288.9 eV) on CeO$_{2-x}$, the formation of carbonate appears more likely. The presence of carbonate and methoxy species suggests partial C–C bond cleavage upon adsorption of acetic acid on highly active vacancy sites (e.g., step edges) of partially reduced CeO$_{2-x}$/, even at 150 K. As on stoichiometric CeO$_2$(111), the intensities of the molecular peaks (2) and (2$'$) are very similar, suggesting random orientation of molecularly adsorbed acetic acid on CeO$_{2-x}$. During acetic acid adsorption, the peak (3) shifts to 287.5 eV while its intensity decreases. This may suggest either attenuation or displacement of methoxy by acetic acid. The variation of the binding energy of methoxy has been observed earlier and was related to the presence of coadsorbates on reduced CeO$_{2-x}$. Note that the binding energies corresponding to acetate and acetic acid species on the partially reduced ceria surface are higher compared to those on stoichiometric ceria. A similar behavior was observed for other oxygenates on ceria surfaces as well.
and (i') is observed, similar to stoichiometric CeO$_2$. Decomposition of the acetate is observed above 350 K. The reaction gives rise to complex spectra, indicating simultaneous formation of numerous surface species. Corresponding C 1s peaks primarily emerge at 284.9 eV (4), 288.6–289.5 eV (5), and 286.0 eV (6). We assign these peaks to carbon, formate, and C$_2$H$_4$, respectively. At the same time, we observe an increase of the peak (3) earlier assigned to methoxy.

Selected TPD spectra obtained from CeO$_2$$_{m/z}$ (red lines) are compared with the spectra from CeO$_2$(111) (black lines) in Figure 3. Similar to CeO$_2$(111), the major products below 250 K are acetic acid, ketene, and acetaldehyde. Molecular acetic acid ($m/z = 43, 60$) desorbs at 196 K followed soon by ketene ($m/z = 14$), acetaldehyde ($m/z = 29, 43, 44$), water ($m/z = 18$), CO ($m/z = 28$), and H$_2$ ($m/z = 2$) at 200 K. Similar to stoichiometric CeO$_2$ film, the comparison of the $m/z$ ratios at 14, 29, and 45 yielded 53% of ketene, 16% of acetaldehyde, and 31% of molecular acetic acid.

The most important differences in decomposition of acetate on CeO$_2$(111) and CeO$_2$_{$m/z$} become apparent at temperatures above 450 K. Specifically, we observe suppression of ketene production at 506 K along with desorption of water, CO, CO$_2$, and ethylene at this temperature. This is consistent with preferential C–O bond cleavage in acetate resulting in partial reoxidation of CeO$_2$_{$m/z$} (see Figure 2f) and formation of C$_2$H$_4$ species (see Figures 1b and 2e). It appears, however, that acetaldehyde desorption at 506 K is hardly affected. Acetaldehyde desorbs in a broad peak between 510 and 587 K. Unlike on CeO$_2$(111), acetone desorption is strongly suppressed. Instead, we observe desorption of methanol at 565 K. The complete list of products is given in Table 1. Additionally, we provide more details on the analysis of the TPD spectra in the Supporting Information.

Desorption of methanol and the formation of formate and methoxy indicate C–C and C–O bond scission in acetate. However, a large amount of carbon is formed on the reduced CeO$_2$_{$m/z$} film that is not removed by annealing to 700 K. A similar observation has been reported for CeO$_2$_{$m/z$}/Ru(0001) by Mullins et al.

### 3.3. Adsorption and Decomposition of Acetic Acid on Pt/CeO$_2$

Interestingly, decomposition of acetic acid on Pt particles supported on CeO$_2$(111)/Cu(111) films strongly differs from both CeO$_2$(111)/Cu(111) (see Section 3.1) and Pt(111)$_{m/z}$ surfaces. Selected TPD spectra obtained from Pt/CeO$_2$(111) exposed to 15 L of acetic acid at 150 K are plotted in Figure 4 in comparison to CeO$_2$(111). The major desorption products on Pt/CeO$_2$(111) are hydrogen ($m/z = 2$) and CO ($m/z = 28$). Hydrogen desorbs in two peaks at 298 and 503 K. Desorption of hydrogen at 298 K is not accompanied by any other products. Therefore, we assume that the hydrogen desorption at 298 K results from deprotonation of acetic acid. Surprisingly, the hydrogen desorption from Pt(111) occurs at 375 K, which is 77 K higher than on Pt/CeO$_2$. The second intense desorption peak of hydrogen at 503 K does not exist either on Pt(111) or CeO$_2$(111). Desorption of CO and traces of formaldehyde accompany hydrogen at this temperature. In contrast to CeO$_2$(111), where the amounts of CO and CO$_2$ are comparable, a significantly larger amount of CO forms on Pt/CeO$_2$(111). This clearly points to preference for the decarbonylation pathway.

![Figure 4](image.png)

The desorption profile of CO$_2$ on Pt/CeO$_2$(111) is similar to that on CeO$_2$(111), but the complete spectrum is shifted to lower temperature on Pt/CeO$_2$(111) by as much as 95 K. Desorption of ketene and acetone is strongly suppressed on Pt/CeO$_2$. Small amounts of water accompanied by traces of methanol and acetaldehyde desorb at 480 K. Unlike on stoichiometric CeO$_2$(111), we did not observe desorption of hydrocarbons (i.e., ethylene and acetylene) from Pt/CeO$_2$(111). Neither did we detect any desorption of methane as in the case of Pt(111). The TPD spectrum at $m/z = 16$ is similar to the one at $m/z = 44$ suggesting that it is due to CO$_2$ desorption only. We note that desorption of methane occurs in parallel to hydrogen desorption from Pt(111) at 375 K. Earlier, we also observed simultaneous desorption of hydrogen and methane during decomposition of formic acid on Pt/CeO$_2$(111). The absence of methane desorption from Pt/CeO$_2$(111) suggests that acetic acid does not decompose to atomic carbon below 375 K on Pt particles. A complete list of desorption products is given in Table 2.
Exposure to 15 L of Acetic Acid at 150 K

The methyl groups in acetate and molecular acetic acid on CeO2 as a function of temperature. Again, only the intensities of the integrated intensities of the C 1s peaks are plotted in Figure 6b to 15 L of acetic acid at 150 K are shown in Figure 5a. The peaks (8) and (8′) from both CeO2 and Pt particles. Analysis of the TPD spectra exposure and temperature in Supporting Information (see Figure 6c). Decomposition of hydroxyl groups above 250 K followed by reverse hydrogen spillover gives rise to the hydrogen desorption at 298 K discussed above. The hydrogen spillover would free up the reactive sites for further decomposition of molecularly adsorbed acetic acid to acetate on Pt. An alternative explanation could be related to the presence of the small number of Ce3+ ions formed upon deposition of Pt particles on CeO2(111) film.47 This effect is reflected in the increase of RER from 0 (CeO2) to about 0.8 (Pt/CeO2). Note that Ce3+ ions are also created upon hydrogen spillover from Pt. As shown below (see Figure 2e), the amount of acetate during annealing on the partially reduced ceria (i.e., in the presence of Ce3+). In the next section, we will, however, show that increased acetate coverage on CeO2 is primarily caused by spillover of the acetate species from the Pt particles.

The peak from acetate on Pt disappears at 225 K. At 200 K, we resolved two new components emerging at 289.7 (2′), 289.8 (8′), 286.1 (2′), and 285.6 eV (8). The peaks (2) and (2′) are assigned to acetic acid on CeO2, while the peaks (8) and (8′) correspond to acetic acid on the Pt particles.

Integrated intensities of the C 1s peaks are plotted in Figure 6a as a function of acetic acid exposure. For acetates and molecular acetic acid, only the intensities of the methyl groups are shown. After adsorption of 15 L of acetic acid on Pt/CeO2 at 150 K, the C 1s spectrum is dominated by the molecularly adsorbed acetic acid on Pt particles.

C 1s spectra obtained during annealing of Pt/CeO2 exposed to 15 L of acetic acid at 150 K are shown in Figure 5a. The integrated intensities of the C 1s peaks are plotted in Figure 6b as a function of temperature. Again, only the intensities of the methyl groups in acetate and molecular acetic acid on CeO2 and Pt are shown. Additionally, we show evolution of Pt 4f binding energy on Pt/CeO2 as a function of acetic acid exposure and temperature in Supporting Information (see Figure S3).

Annealing to 200 K removes molecularly adsorbed acetic acid from both CeO2 and Pt particles. Analysis of the TPD spectra in the region below 250 K suggests desorption of acetic acid (m/z = 43, 60) at 194 K followed by ketene (m/z = 14), acetaldehyde (m/z = 29, 43, 44), water (m/z = 18), CO (m/z = 28), and H2 (m/z = 2) at 197 K.

Table 2. Desorbing Products Observed during TPD from Pt/CeO2(111)/Cu(111) and O/Pt/CeO2(111)/Cu(111) Following Exposure to 15 L of Acetic Acid at 150 K

<table>
<thead>
<tr>
<th>T [K]</th>
<th>194</th>
<th>197</th>
<th>298</th>
<th>410</th>
<th>480</th>
<th>495</th>
<th>503</th>
<th>645</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/CeO2(111)</td>
<td>CH3COOH</td>
<td>CH3CHO</td>
<td>CH2H2O</td>
<td>CH2OH</td>
<td>H2</td>
<td>CO2</td>
<td>CO2</td>
<td>CO2</td>
</tr>
<tr>
<td>O/Pt/CeO2(111)</td>
<td>CH2COOH</td>
<td>CH3OH</td>
<td>CO</td>
<td>H2</td>
<td>CO2</td>
<td>CH2H2O</td>
<td>H2</td>
<td>CH2H2O</td>
</tr>
</tbody>
</table>

The products designated in bold represent majority species at each desorption temperature.

The analysis of the surface species identified by SRPES helps us understand the decomposition mechanism of acetic acid on Pt/CeO2(111).

C 1s spectra obtained from Pt/CeO2 during adsorption of acetic acid at 150 K are shown in Figure 5a. We took advantage of the different binding energy splitting between the methyl and carboxylate/carboxyl groups in the acetate and acetic acid adsorbed on Pt(111)14 and CeO2(111) to identify adsorption sites on Pt/CeO2(111). Naturally, the measured spectra are rather complex. At low doses of acetic acid, peaks are resolved at 288.5 (1), 285.24 (1), 289 (7), 284.8 (7), 287.5 (9), 286.75 (10), and 286.2 eV (11). The features (1) and (1′) are assigned to acetate on CeO2. The peaks (7) and (7′) are attributed to acetate on the Pt nanoparticles. The features (9), (10), and (11) are associated with methoxy and with CO adsorbed on the Pt particles in on-top and bridge positions, respectively. Minor spectral features at 283.5 (12) and 284.0 eV (13) represent ethylene and ethyldiene adsorbed on Pt particles, respectively.14 At higher doses of acetic acid, four additional peaks emerge at 289.7 (2′), 289.8 (8′), 286.1 (2′), and 285.6 eV (8). The peaks (2) and (2′) are assigned to acetic acid on CeO2, while the peaks (8) and (8′) correspond to acetic acid on the Pt particles.

Unlike on stoichiometric CeO2(111)/Cu(111) and Pt(111),14 the intensities of acetates on Pt/CeO2 increase on both Pt particles and CeO2 substrate. This observation suggests that annealing triggers the migration of the adsorbed acetic acid to reactive sites, giving rise to additional acetate, hydroxyl groups (on CeO2), and coadsorbed hydrogen (on Pt). Because the saturation amount of acetate on Pt(111) is already formed upon adsorption at 150 K,14 we believe that the remaining reactive sites on Pt(111) were occupied by other adsorbates or products (e.g., by hydrogen). Unlike on Pt(111), spillover of hydrogen atoms from the Pt particles to the ceria substrate occurs on Pt/CeO2.57 The hydrogen spillover causes partial reduction of cerium oxide upon formation of hydroxyl groups, as evident from the increase of the RER between 160 and 250 K (see Figure 6c). Decomposition of hydroxyl groups above 250 K followed by reverse hydrogen spillover gives rise to the hydrogen desorption at 298 K discussed above. The hydrogen spillover would free up the reactive sites for further decomposition of molecularly adsorbed acetic acid to acetate on Pt. An alternative explanation could be related to the presence of the small number of Ce3+ ions formed upon deposition of Pt particles on CeO2(111) film.47 This effect is reflected in the increase of RER from 0 (CeO2) to about 0.8 (Pt/CeO2). Note that Ce3+ ions are also created upon hydrogen spillover from Pt. As shown below (see Figure 2e), the amount of acetate increases during annealing on the partially reduced ceria (i.e., in the presence of Ce3+). In the next section, we will, however, show that increased acetate coverage on CeO2 is primarily caused by spillover of the acetate species from the Pt particles.

The peak from acetate on Pt disappears at 225 K. At 200 K, we resolved two new components emerging at 289.3 (18) and 285.4 eV (18). The corresponding peaks (18) and (18′) represent new acetate species on the CeO2 substrate. It is noteworthy that these acetates are characterized by a substantially larger binding energy splitting (3.8–3.9 eV) between the methyl and carboxylate groups than those observed for acetate on pure CeO2(111) (3.4 eV). We label this acetate species as "acetate*". During annealing, all acetates are converted to acetate*.

The spillover of acetate from the Pt particles to ceria results in an increased surface density, in other words a "surface crowding" of the acetate species on the CeO2 support. Simultaneously with this process, we observe a change in the
binding energy splitting in the acetate from 3.4 eV (acetate) to 3.8–3.9 eV (acetate*). This effect may be associated with a change of adsorption geometry, specifically the transition from bidentate to monodentate adsorption geometry. For example, acetate in monodentate configuration on TiO$_2$(011)–$2 \times 1$ has a splitting of 4.1 eV, whereas a smaller splitting of 3.6 eV has been reported for the bidentate acetate on TiO$_2$(110).

It is noteworthy that the thermal stability of methoxy on Pt/CeO$_2$ is higher than that on Pt(111). This species completely disappears from Pt/CeO$_2$ at 500 K. Therefore, we suggest that a fraction of the methoxy migrates onto the ceria support, where it is bound more strongly and is stabilized up to this temperature.

During annealing, the amount of carbonaceous deposits on the Pt particles increases, as indicated by the increasing intensity of the peaks (13) and (14) at 284.4 eV (see Figure 5a). Above 450 K, the peaks (13) and (14) are accompanied by the peak (4). The latter emerges at 285 eV and is associated with carbon adsorbed on reduced ceria. A similar species is found during decomposition of acetic acid on partially reduced ceria (see Section 3.2). Note that in this temperature range oxygen reverse spillover is activated which can lead to reduction of ceria and to formation of oxygen vacancies. In Figure 6b, the summed contribution from carbonaceous and hydrocarbon species is shown. The accumulation of surface carbon reaches a maximum at 450 K. Above this temperature, the amount of the carbon decreases until it is completely removed from Pt/CeO$_2$ at 750 K. Removal of surface carbon from the Pt particles occurs by reverse spillover of oxygen from ceria to the Pt nanoparticles and subsequent recombination with the carbonaceous species.

Figure 5. C 1s spectra obtained from Pt/CeO$_2$(111) (a) and O/Pt/CeO$_2$ (b) during adsorption of acetic acid at 150 K followed by stepwise annealing.
Interestingly, the carbon deposits from the ceria support are removed on Pt/CeO₂ above 600 K. This is in sharp contrast to Pt-free CeO₂−ₓ, where these carbonaceous species were not removed, even during annealing up to 700 K.

In summary, the intrinsic properties of Pt/CeO₂ films (i.e., the occurrence of the spillover phenomena) resulted in a unique decomposition mechanism of acetic acid that is different from those observed on Pt(111) and Pt-free CeO₂. In this respect, the catalyst morphology consisting of Pt nanoparticles in contact with cerium oxide is vital for the occurrence of acetate crowding.

However, annealing of Pt/CeO₂ film above 750 K leads to a slight reduction of cerium oxide and may activate strong metal-support interaction (SMSI), resulting in a partial encapsulation of supported Pt particles by oxide. We discuss the effect of the high-temperature treatment of Pt/CeO₂ on the decomposition of acetic acid in Supporting Information.

### 3.4. Adsorption and Decomposition of Acetic Acid on O/Pt/CeO₂

C 1s spectra obtained from O/Pt/CeO₂ during Figure 6. Integrated intensities of C 1s spectral components (a, b, d, e) and RER (c, f) as a function of exposure (a, d) and temperature (b, c, e, f) on Pt/CeO₂(111) (a–c) and O/Pt/CeO₂ (d–f). The C 1s spectra were acquired with hν = 410 eV. For clarity, the (2') component is not plotted in (a, b, d, e) as it is equal in intensity to (2).

Interestingly, the carbon deposits from the ceria support are removed on Pt/CeO₂ above 600 K. This is in sharp contrast to Pt-free CeO₂−ₓ, where these carbonaceous species were not removed, even during annealing up to 700 K.

In summary, the intrinsic properties of Pt/CeO₂ films (i.e., the occurrence of the spillover phenomena) resulted in a unique decomposition mechanism of acetic acid that is different from those observed on Pt(111) and Pt-free CeO₂. In this respect, the catalyst morphology consisting of Pt nanoparticles in contact with cerium oxide is vital for the occurrence of acetate crowding.

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adsorption of acetic acid at 150 K are shown in Figure 5b. The spectra were fitted using the same approach as for Pt/CeO₂ (see Section 3.3). The species are assigned in accordance with those found on Pt/CeO₂. Consequently, the peaks (1) and (1') at 284.9 eV and 288.3 are attributed to acetate on CeO₂. The peaks (7) and (7') at 284.7 and 288.9 eV are assigned to acetate on the Pt particles. Peaks (10) and (11) at 286.9 and 286.2 eV correspond to CO adsorbed on on-top and bridge sites on Pt particles. In contrast to Pt/CeO₂, the peak (9) at 287.5 eV, earlier assigned to methoxy, very likely contains a contribution from the acetyl species on O/Pt/CeO₂. Previously, we reported that acetyl is the dominant species formed upon adsorption of acetic acid on oxygen pre-exposed Pt(111).14 In view of the high complexity of C 1s spectra on O/Pt/CeO₂, we cannot resolve the contribution from the methyl group in the acetyl. The peaks (2) and (2') at 285.5 and 289.2 eV, respectively, are assigned to acetic acid on CeO₂. The peaks (8) and (8') at 285.5 and 289.5 eV, respectively, correspond to acetic acid on the Pt particles. Additionally, we show evolution of Pt 4f binding energy on O/Pt/CeO₂ as a function of acetic acid exposure and temperature in Supporting Information (see Figure S3).

The amount of acetate formed on the oxygen pre-exposed Pt particles (i.e., on O/Pt/CeO₂) is larger than on the oxygen-free Pt particles (Pt/CeO₂). Previously, it was suggested that atomic oxygen acts as a Brønsted base that promotes the formation of acetate.20

The integrated C 1s intensities of the species formed on O/Pt/CeO₂ are plotted in Figure 6d as a function of acetic acid exposure. For clarity, only the intensities of the methyl groups in acetates and acetic acid on CeO₂ and Pt particles are shown. Similar to Pt/CeO₂, the C 1s spectrum obtained from O/Pt/CeO₂ after exposure to 15 L of acetic acid at 150 K is dominated by the molecular acetic acid adsorbed on the Pt particles.

The integrated intensities of the C 1s peaks are plotted in Figure 6c as a function of temperature. Again, only the intensities of the methyl carbon in acetate*/acetate and acetic acid on CeO₂ and Pt are shown. As on Pt/CeO₂, desorption of molecular acetic acid from CeO₂ and Pt occurs below 225 K. Also, the amount of acetates on Pt and CeO₂ increases upon annealing to 160 and 200 K, respectively. The acetate vanishes from Pt at 250 K. Above 200 K, we detected formation of acetate* represented by the peaks (18) and (18'). Similarly to Pt/CeO₂, all acetate is converted to acetate* during annealing. The evolution of the summed intensities of the peaks (12), (13), (14), (15), and (4) associated with ethylene (12), ethylidene (13), ethylidyne (14), carbon on Pt (15), and carbon on CeO₂-x (4) is similar to that observed on Pt/CeO₂. Accumulation of surface carbon on O/Pt/CeO₂ is completed between 425 and 450 K. Between 475 and 700 K, all carbonaceous deposits are removed from the surface, similarly to Pt/CeO₂. The thermal behavior of methoxy/acytel and CO is also similar to Pt/CeO₂. The peak intensities related to these species do not increase during annealing. The corresponding peaks (9), (10), and (11) decrease gradually until they vanish from the C 1s spectra around 450 K.

Similarly to Pt/CeO₂, we observed a significant increase of the acetate concentration on CeO₂ support during annealing to 200 K on O/Pt/CeO₂ (see Figure 6e). The observation of this effect on both Pt/CeO₂ and O/Pt/CeO₂ suggests that it is not associated with the degree of ceria reduction. As discussed above, a small amount of Ce³⁺ centers is formed on stoichiometric CeO₂ immediately upon deposition of Pt.37 Typically, it results in an increase of the RER from 0 (CeO₂) to 0.7–0.8 (Pt/CeO₂). However, O₂ exposure and annealing during preparation of O/Pt/CeO₂ causes reoxidation of Ce³⁺ centers. As a result, we obtain a RER which is very close to 0 on O/Pt/CeO₂ (see Figure 6f). Another difference between the Pt/CeO₂ and the O/Pt/CeO₂ sample is the suppression of hydrogen spillover on O/Pt/CeO₂. As discussed in Section 3.3, hydrogen spillover from Pt particles to the CeO₂ substrate results in an increase of the RER between 160 and 250 K (see Figure 6c). At higher temperature, reverse hydrogen spillover results in a decrease of RER to its initial value.57 The comparison of the RERs on Pt/CeO₂ (Figure 6c) and O/Pt/CeO₂ (Figure 6f) reveals that hydrogen spillover does not occur on O/Pt/CeO₂. This assumption is supported by the comparison of the TPD spectra obtained from O/Pt/CeO₂ (red lines) and Pt/CeO₂ (black lines) exposed to 15 L of acetic acid at 150 K (see Figure 7). It is evident that no hydrogen desorption occurs at 298 K on O/Pt/CeO₂.

Figure 7. Selected TPD spectra obtained from Pt/CeO₂(111)/Cu(111) (black lines) and O/Pt/CeO₂(111)/Cu(111) (red lines) films exposed to 15 L of acetic acid at 150 K. The spectra in the left and right panels are scaled with respect to the top spectrum (m/z = 2).
Besides the generally lower intensity of several TPD peaks on O/Pt/CeO₂, we note several additional differences related to the coadsorbed oxygen. In particular, we observe double peak structures in the desorption spectra of all measured m/z ratios below 250 K. The first set of products starts with the desorption of acetic acid (m/z = 43, 45, 60) at 166 K followed shortly after by desorption of ketene (m/z = 14), acetaldehyde (m/z = 29, 43, 44), water (m/z = 18), CO (m/z = 28), and H₂ (m/z = 2) at 174 K. Similar to Pt/CeO₂, the second set of products starts with the desorption of acetic acid at 194 K followed by desorption of ketene, acetaldehyde, water, CO, CO₂, and H₂ at 197 K.

Desorption and decomposition of acetic acid at 166–174 K is most likely related to the formation of multilayer acetic acid on O/Pt/CeO₂. For instance, Gao and Hemminger²² reported desorption of acetic acid at 178 K from Pt(111). In contrast, we did not observe desorption of acetic at this temperature either on Pt(111) or O/Pt(111) (after exposure to 15 L of acetic acid at 150 K).¹⁴ Instead we find desorption and decomposition of acetic acid at 222 K. Above 250 K, the differences between Pt/CeO₂ and O/Pt/CeO₂ include additional desorption of CO₂ at about 287 K, ketene and acetic acid at 365 K, and water at 380 K. The products desorbing at 365–380 K are similar to the decomposition channel on oxygen pre-exposed Pt(111) at 390 K, and the only difference is related to the absence of methane on O/Pt/CeO₂. Therefore, we assume that these additional products are most likely formed on the surface of Pt particles.

4. CONCLUSIONS

We have studied the adsorption and reaction of acetic acid on a Pt/CeO₂(111)/Cu(111) model catalyst by means of SRPES, RPES, and TPD. In order to assign the spectral features, we have performed additional experiments on stoichiometric CeO₂(111)/Cu(111), partially reduced CeO₂−x/Cu(111), and O/Pt/CeO₂(111)/Cu(111) under identical conditions.

1. Adsorption of acetic acid at 150 K yielded acetate species coadsorbed with molecular acetic acid on all surfaces. In comparison to Pt/CeO₂(111)/Cu(111), a higher amount of acetate is formed on O/Pt/CeO₂(111)/Cu(111). This is related to the promoting role of basic sites (i.e., coadsorbed oxygen on Pt particles) in acetate formation. Desorption of molecular acetic acid between 194 and 200 K is accompanied by formation of ketene, acetaldehyde, water, CO, and H₂, as well as traces of CO₂ and methanol. Additionally, desorption of weakly bound acetic acid is detected on O/Pt/CeO₂(111)/Cu(111) between 166 and 174 K.

2. Acetates on stoichiometric CeO₂(111)/Cu(111) are stable up to 425 K. Annealing of the sample does not result in an increase of the amount of acetate on CeO₂(111)/Cu(111). The formation of acetate is accompanied by hydroxyl groups that give rise to desorption of water at about 300 K. At this temperature, the desorption of water does not cause reduction of CeO₂(111)/Cu(111). The major products of acetate decomposition on CeO₂(111)/Cu(111) include CO, CO₂, ketene, and water desorbing at two characteristic temperatures, 506 and 589 K. Additionally, desorption of CO, CO₂, and water occurs at 609 K. Numerous minor products such as acetaldehyde, acetone, C₂H₄, and C₂H₂ were also detected.

3. On partially reduced CeO₂−x/Cu(111), acetates are stable up to 450 K. Annealing of the sample results in an increase of the amount of adsorbed acetate. Unlike on stoichiometric CeO₂(111), desorption of water does not occur at 300 K on CeO₂−x. In comparison to the stoichiometric CeO₂(111) films, the amounts of CO and particularly CO₂ are lower on CeO₂−x. Production of ketene occurs only at 589 K. We assume that suppression of the decomposition channel at 506 K is related to CO bond scission in the acetate that gives rise to reoxidation of CeO₂−x and formation of strongly adsorbed C₂H₄ species. As a result, a considerable amount of carbon is left on CeO₂−x after annealing to 700 K. Besides acetaldehyde, acetone, C₂H₄, and C₂H₂, side products are formed which include methanol and formaldehyde.

4. Adsorption of acetic acid on Pt/CeO₂(111)/Cu(111) leads to the formation of acetate and molecular acetic acid on both Pt particles and on ceria at 150 K. The relative amounts of these species on Pt and ceria have been determined from the C 1s spectra taking advantage of the specific binding energy splitting between the methyl and the carboxyl/carboxylate groups in acetate and acetic acid on CeO₂ and on Pt(111), respectively. Using this information in the fitting procedure, we obtain insight into the specific stabilities and decomposition mechanism of acetate on Pt/CeO₂(111)/Cu(111).

5. Specifically, we find an increase of acetate concentration on ceria between 150 and 200 K. This effect results from deprotonation of molecularly adsorbed acetic acid to acetate followed by its spillover from the Pt particles to the support. The increased acetate concentration on ceria leads to formation of an acetate species with a different adsorption geometry, i.e. monodentate acetate, above 250 K. Decomposition of these species yields large amounts of hydrogen and CO. The formation of ketene and acetone is largely eliminated. Hydrogen desorbs in two peaks at 298 and 503 K.

6. Adsorption and decomposition of acetic acid on O/Pt/CeO₂(111)/Cu(111) proceeds via similar species as observed on Pt/CeO₂(111)/Cu(111). The coadsorbed oxygen has several effects: (a) reoxidation and elimination of Ce³⁺ formed upon Pt deposition; (b) suppression of hydrogen spillover and, therefore, suppression of hydrogen desorption at 289 K; (c) formation of ketene, CO₂, and water at 365–380 K as a product of adsorbate decomposition on the Pt particles.

The decomposition of acetate on Pt/CeO₂(111)/Cu(111) and O/Pt/CeO₂(111)/Cu(111) leads to carbon deposition on Pt particles and on the ceria support. These carbon deposits are removed by thermal treatment. The self-cleaning process is related to reverse oxygen spillover from the ceria support to the Pt particles on Pt/CeO₂ activated above 450 K. In sharp contrast to Pt-free CeO₂−x, even the carbon deposits from the ceria support can be oxidatively removed from Pt/CeO₂ above 600 K. A similar behavior during thermally induced self-cleaning is observed on both Pt/CeO₂(111) and O/Pt/CeO₂(111).
ASSOCIATED CONTENT

Supporting Information
Additional description of supplemental data as noted in the text. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b03079.

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Notes
The authors declare no competing financial interest.

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ABBREVIATIONS

SRPES, synchrotron radiation photoelectron spectroscopy; RPES, resonant photoemission spectroscopy; RER, resonant enhancement ratio; TPD, temperature-programmed desorption; QMS, quadruple mass spectrometer; LEED, low energy electron diffraction; UHV, ultrahigh vacuum

REFERENCES
