Water Chemistry on Model Ceria and Pt/Ceria Catalysts

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ABSTRACT: We have studied the interaction of water with stoichiometric CeO2(111)/Cu(111), partially reduced CeO2−x/Cu(111), and Pt/CeO2/Cu(111) model catalysts by means of synchrotron-radiation photoelectron spectroscopy (SRPES), resonant photoemission spectroscopy (RPES) at the Ce 4d edge, infrared reflection absorption spectroscopy (IRAS), and density functional (DF) calculations. The principal species formed during adsorption of water at 160 K on CeO2(111) films is chemisorbed molecular water. On the surface of CeO2−x, water partially dissociates yielding hydroxyl groups. By use of core-level PES, differentiation between chemisorbed water and hydroxyl groups is complicated by the overlap of the corresponding spectral features. Nevertheless, we determined three characteristic indicators for OH groups on ceria: (i) the presence of 1σ and 3σ states in valence band (VB) PES; (ii) an increase of the binding energy (BE) separation between the O 1s spectral components of lattice oxygen and OH/H2O; (iii) an increase of the amplitude of the Ce3+ resonance in RPES. Chemisorbed water desorbs below 400 K and hydroxyl groups vanish at 500 K. The most favorable configurations of chemisorbed water and hydroxyl groups have been investigated by DF calculations. Both CeO2(111) and CeO2−x involve strongly tilted H2O and OH species which complicate their detection by IRAS. On Pt/CeO2, water adsorbs molecularly at 160 K but undergoes partial dissociation during annealing. The dissociation of water is accompanied by spillover of hydrogen to ceria and formation of hydroxyl groups between 180 and 250 K. Above 250 K, decomposition of hydroxyl groups and reverse spillover of hydrogen from ceria to Pt occurs, followed by desorption of molecular water.

1. INTRODUCTION

Microscopic understanding of the water interaction with ceria-based catalysts has significant implications for numerous chemical processes, e.g., the steam reforming of hydrocarbons or the water gas shift (WGS) reaction. The fundamental aspects of the water interaction with various solid surfaces has been reviewed in detail, e.g., by Thiel and Madey1 and by Henderson.2 In general, it was reported that water interacts more strongly with oxide surfaces compared to noble metal surfaces. On most metal oxide surfaces, water interacts with the cation site via its 3a1 orbital. Depending on the structure and stoichiometry of the oxide, the water molecule may then adsorb either molecularly or dissociatively.1,2

On the stoichiometric CeO2(111) surface, water molecules adsorb above cerium ions3–5 without dissociation, and Kumar and Shelling6 predicted tilted adsorption geometries of the water molecule based on density functional (DF) calculations. As a result, the water molecule forms single3,7 or double1 hydrogen bonds with surface oxygen ions. Dissociation of water occurs on reduced or partially reduced CeO2−x surfaces.8–12 It has been suggested that the water molecule dissociates forming OH groups, which fill the oxygen vacancies and are hydrogen bound to surface oxygenen.8–10 Filling of oxygen vacancies by hydroxyl groups on ceria has been confirmed experimentally by Gritschneder and Reichling4 using dynamic atomic force microscopy. However, discrepancies remain in the literature.

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regarding the impact of water on the cerium oxidation state. For instance, Kundakovic et al. reported desorbed $\text{H}_2$ to be the main product of irreversible water dissociation on reduced ceria on Ru(0001), but they observed no significant alteration of the oxidation state of cerium, neither upon adsorption nor desorption. In contrast, Henderson et al. reported that dissociation of water on reduced ceria on yttria-stabilized ZrO$_2$(111) is reversible, i.e., occurs without release of $\text{H}_2$ into the gas phase. The authors attributed weak reduction of ceria upon water adsorption at elevated temperatures to redistribution of oxygen vacancies from the bulk to the surface. Berner et al. observed reduction of noncontinuous CeO$_2$ deposits on Pt(111) during adsorption of water at 300 K without significant formation of hydroxyl groups. An apparent reduction of ceria induced by water has also been observed on stoichiometric CeO$_2$(111) films on Cu(111) by Matofin et al. The authors suggested that the water molecule triggers a redistribution of charge within the cerium ion, yielding a charge depletion in 5d and a charge accumulation in 4f states. DF studies imply another explanation of the observed effect: they predict a strong attractive interaction between water and bulk oxygen vacancies, causing rapid diffusion of vacancies to the surface. Both experimental and theoretical studies agree that water tends to reduce rather than reoxidize ceria, at least for the systems and conditions investigated.

Dissociation of water on noble metal surfaces occurs less readily. Shvorovsky et al. investigated the reactivity of water on hexagonal Pt-group metals and found higher reactivity for the 4d metals (Ru, Rh, Pd) as compared to 5d (Ir, Pt). Generally, Pt(111) and Pt stepped surfaces are considered particularly inert toward water dissociation. However, adding a small amount of oxygen to the surface facilitates dissociation of water on Pt(111). In the presence of thick ice layers, the dissociation of a buried monolayer of water on Pt(111) has also been reported.

Establishing whether a water molecule adsorbs molecularly or dissociatively on the catalyst’s surface may represent a challenge to many surface diagnostic tools. The problems arise from many similarities in the properties of molecular H$_2$O and OH species or from overlaps of distinctive spectral features, e.g., in photoelectron spectroscopy. Characterization of mixed molecular and dissociative adsorption is especially difficult in the case of reversible dissociation.

In this paper, we perform a comprehensive study of water adsorption and dissociation on well-ordered stoichiometric CeO$_2$(111), partially reduced CeO$_{2-x}$, and Pt/CeO$_2$(111) model catalysts prepared on Cu(111) single crystal. We combine synchrotron radiation photoelectron spectroscopy (SRPES), resonant photoemission spectroscopy (RPES), and infrared reflection absorption spectroscopy (IRAS) with DF calculations. The complementarity of these methods largely resolves the above-mentioned difficulties and provides insight into the water chemistry on ceria based catalysts and the related redox processes.

2. EXPERIMENTAL METHODS

2.1. SRPES and RPES. High-resolution SRPES was performed at the Materials Science Beamline at the Elektra synchrotron facility in Trieste, Italy. The radiation source was a bending magnet producing synchrotron light in the energy range of 21–1000 eV. The ultrahigh vacuum (UHV) endstation (base pressure $1 \times 10^{-10}$ mbar) was equipped with a multichannel electron energy analyzer (Specs Phoibos 150), a rear-view low-energy electron diffraction (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 used for energy calibration of the synchrotron light and for off-line work. Additionally, two electron-beam evaporators for Ce and Pt deposition were installed. A single crystal Cu(111) disk (MaTeK GmbH, 99.999%) was used as a substrate for CeO$_2$(111), CeO$_{2-x}$, and Pt/CeO$_2$(111). First, 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 layers of CeO$_2$ were prepared on clean Cu(111) by physical vapor deposition (PVD) of Ce metal (Goodfellow, 99.99%) in an oxygen atmosphere ($p_{\text{O}_2} = 5 \times 10^{-7}$ 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 10 min. The preparation method yields a continuous, stoichiometric CeO$_2$(111) film with a thickness in the range of 1.9–2.1 nm as determined from the attenuation of the Cu LP$_{3/2}$ intensity. LEED observations of the prepared films confirm the epitaxial growth of CeO$_2$(111) with the characteristic (1.5 $\times$ 1.5) superstructure relative to the Cu(111) substrate. According to previous scanning tunneling microscopy (STM) studies, flat CeO$_2$(111) terraces are separated by steps and contain extended rough patches composed of small ceria particles. Partially reduced ceria film (CeO$_{2-x}$) was prepared by exposing a stoichiometric CeO$_2$(111) film to 45 L (Langmuir, 1 L = 1.33 $\times$ 10$^{-6}$ mbar x s) of methanol by backfilling the chamber at a sample temperature of 700 K, followed by annealing at 700 K in UHV for 30 min. The procedure yields partially reduced CeO$_{2-x}$ films, where $x = 0.16$. Pt was deposited by means of PVD from a Pt wire (0.5 mm in diameter, Goodfellow, 99.99%) onto CeO$_2$/Cu(111) at 300 K. The nominal thickness of the deposited Pt layer was 0.4 nm as determined from the attenuation of the Cu LP$_{3/2}$ intensity. The structure and thermal stability of the Pt/CeO$_2$ systems have been discussed before. Briefly, Pt nanoparticles grown at 300 K preferentially nucleate at rough patches of the ceria surface. Typically, the density of Pt particles is (5.4 $\pm$ 1.0) $\times$ 10$^{23}$ cm$^{-2}$, and the average size of Pt particles is 3.3 $\pm$ 0.3 nm for the Pt/CeO$_2$ system with a nominal thickness of the Pt deposit of 0.5 nm.

VB spectra were acquired at three different photon energies (PES), 121.4, 124.8, and 115.0 eV, that 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. Core level spectra of O 1s, C 1s, and Pt 4f were acquired at 650, 410, and 180 eV, respectively. The BEs in the spectra acquired with synchrotron radiation were calibrated with respect to the Fermi level. Additionally, Al K$_\alpha$ radiation (1486.6 eV) was used to measure the core levels of O 1s, C 1s, Pt 4f, Ce 3d, and Cu 2p$_{3/2}$. 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. The total spectral resolutions achieved were 1 eV (Al K$_\alpha$), 200 meV (PE = 115–180 eV), 400 meV (PE = 410 eV), and 650 meV (PE = 650 eV). The core level spectra were fitted with a Doniach–Sunjić (DS) function convoluted with Gaussian (Pt 4f) or Voigt (O 1s, C 1s) profiles after proper background subtraction. All SRPES and PES data were processed using KolXPD fitting software.
During the experiment the sample temperature was controlled by a DC power supply passing a current through Ta wires holding the sample. Temperatures were measured by a K-type thermocouple attached to the rear surface of the sample. Stable temperature and fast cooling after the annealing steps were achieved by simultaneous resistive heating and cooling of the manipulator with liquid nitrogen. The investigated samples were exposed in consecutive doses to a total amount of 10^{-11} \text{L} \text{H}_2\text{O} at 160 \text{K} by backfilling the UHV chamber.

### 2.2. Molecular Beams (MB) and IRAS

The MB/IRAS measurements were performed in an UHV apparatus at the Friedrich-Alexander-University Erlangen-Nuremberg, Germany. The setup allows exposure of the sample surface to up to four effusive beams and one supersonic beam. A beam monitor is used that permits exact MB alignment and calibration. In addition, the system is equipped with a vacuum Fourier transform IR (FTIR) spectrometer (Bruker IFS 66/v), two quadrupole mass spectrometers (QMS), a vacuum transfer system, and a high-pressure cell.

A Cu(111) single crystal (MaTeCK GmbH, 99.999%) was used as a substrate for CeO$_2$(111), CeO$_2$–x, and Pt/CeO$_2$ films. Well-ordered CeO$_2$(111) and Pt/CeO$_2$ films were prepared according to the procedures described in section 2.1. The deposition rates of Ce (1.5–2.0 nm per hour) and Pt (0.3 nm per hour) were calibrated using a quartz crystal microbalance (QCM). The resulting thickness of the CeO$_2$(111) film was 1.2–1.5 nm, and the nominal thickness of the deposited Pt layer was 0.4 nm. A partially reduced ceria film (CeO$_2$–x) was produced by means of sputtering of the CeO$_2$(111) film at 300 K with Ar$^+$ ions at energy of 0.7 kV and ion current density 2.5 \mu A/cm$^2$ for 5 min. The procedure results in increased step density and formation of oxygen vacancies on the terraces.

The CeO$_2$(111) and CeO$_2$–x films were exposed to deuterated water, D$_2$O, (Sigma-Aldrich, 99.96%) at 110 K, while Pt/CeO$_2$(111) was exposed to D$_2$ (Linde, 99.9%) at 150 K. The deuterated water was used in order to distinguish between the OH vibrations of the water adsorbed on ceria and the residual water in the IR detector. Both gases, D$_2$O and D$_2$, were dosed via the room-temperature MB nozzle. Argon was used as a carrier gas for D$_2$O, and the amount of D$_2$O in the gas stream calibrated by the QMS and beam monitor was 3.6%.

Pressures of D$_2$ and D$_2$O + Ar at the surface of the samples were 1.2 \times 10^{-6} \text{mbar} and 2.0 \times 10^{-6} \text{mbar}, respectively.

The IR spectra were acquired as follows: First background spectra of the clean samples were taken. Then the samples were exposed to defined doses of D$_2$O using the MB, and then the IR spectrum was recorded. The total exposures of D$_2$O and D$_2$ on the samples were \sim 24 and 50 L, respectively. Finally, the samples were flashed to the desired temperature and cooled down to 110 K again in order to acquire temperature dependent spectra.
2.3. Density Functional Modeling. To model surface complexes on CeO$_2$, we used the plane-wave VASP code$^{24,25}$ employing a generalized gradient approximation (GGA) in the form of the PW91 exchange-correlation functional.$^{26}$ In accord with earlier studies,$^{27–29}$ the Hubbard scheme (GGA+U) with the on-site Coulomb correction $U_{\text{eff}} = 4$ eV was applied to all Ce 4f orbitals to reinforce their localization. The core–valence interaction was treated with the projector augmented wave method (plane wave energy cutoff 415 eV).$^{30,31}$ Because of the considerable size of the unit cell, the calculations were performed only at the $\Gamma$-point of reciprocal space. The total energy threshold defining the self-consistency of the electron density was set to $10^{-4}$ eV and all structures were optimized until forces acting on the relaxed atoms were smaller than 0.2 eV/nm. Spin-polarized calculations were performed when a single H atom was adsorbed on CeO$_2$, while spin-restricted calculations were performed when H$_2$O was adsorbed or dissociated on CeO$_2$. For all optimized structures we determined the relative stability and calculated the harmonic vibrational frequencies that justified their true local energy-minimum character.

We represented the experimentally treated rough ceria surfaces by a model of a stepped CeO$_2$(111) surface.$^{32}$ Step edges running along the (2\bar{1}T) direction were modeled with stoichiometric O–Ce–O stripes located on top of a double-trilayer CeO$_2$(111) slab. To minimize mutual interactions between adjacent steps we used a unit cell that consists of 60 Ce and 120 O atoms (first trilayer, Ce$_3$O$_2$$_{24}$; second and third trilayers, Ce$_{12}$O$_{24}$ each). The size of the unit cell is 1.322 $\times$ 1.984 nm$^2$ with an angle between both directions of 60°. The slabs are separated by more than 1.2 nm of vacuum from their nearest periodic images. The present stepped model has been recently validated by its accurate representation of STM images of nanosilands observed on CeO$_2$(111) films.$^{32}$

3. RESULTS AND DISCUSSION

3.1. Adsorption of Water on Stoichiometric CeO$_2$(111) and Partially Reduced CeO$_{2-x}$ The O 1s core level spectra obtained from stoichiometric CeO$_2$(111)/Cu(111) and partially reduced CeO$_{2-x}$/Cu(111) during exposure to increasing doses of water at 160 K are shown in parts a and b of Figure 1, respectively. The spectra obtained from as-prepared samples at 300 K are shown at the bottom of each figure. The main components in the O 1s spectra at BEs of 529.3 eV (CeO$_2$) and 529.7 eV (CeO$_{2-x}$) emerge due to lattice oxygen anions located near Ce$^{4+}$ cations, O$^{2-}$(Ce$^{4+}$).$^{8,33,34}$ A small contribution from O$^{2-}$ located near Ce$^{3+}$, O$^{2-}$(Ce$^{3+}$), appears at 532.0 eV in the O 1s spectrum obtained from partially reduced CeO$_{2-x}$.$^{34}$ Cooling the samples to 160 K triggers development of an additional small peak at 530.9 eV (CeO$_2$) and growth of the peak at 532.0 eV (CeO$_{2-x}$). These changes are induced by adsorption of water from the residual background gas of the UHV chamber. Subsequent exposure of the samples to water resulted in a further increase of the peaks at 530.9 (CeO$_2$) and 532.0 eV (CeO$_{2-x}$) as well as in the emergence of new peaks at 532.9 eV (CeO$_2$) and 533.5 eV (CeO$_{2-x}$). In parallel, the intensities of the features associated with lattice oxygen are attenuated with increasing doses of water on both samples.

The peaks at 532.9 eV (CeO$_2$) and 533.5 eV (CeO$_{2-x}$) are associated with formation of multilayers of water (ice) on the surfaces of both samples.$^{8,12}$ The individual assignment of the peaks at 530.9 (CeO$_2$) and at 532.0 eV (CeO$_{2-x}$) is less straightforward, however. According to the literature,$^{8}$ either peak may contain contributions from both chemisorbed water (H$_2$O) and hydroxyl groups (OH). As mentioned above,$^{8,12}$ water adsorbs molecularly on stoichiometric CeO$_2$ but undergoes partial dissociation on reduced CeO$_{2-x}$ surfaces.$^{8,10,12}$ BEs of the two surface species are too close to be resolved experimentally.$^{8}$ By use of a nonlinear least-squares fitting procedure, Kundakov et al.$^{13}$ identified two components separated by 0.7 eV on reduced CeO$_2$(111)/Ru(0001). The authors assigned the lower BE component to chemisorbed water and the higher BE component to hydroxyl groups. However, in order to avoid any misinterpretation of the peaks at 530.9 (CeO$_2$) and 532.0 eV (CeO$_{2-x}$), we hereafter assign both peaks to unresolved contributions from chemisorbed water and hydroxyl groups.

The evolution of the integrated intensities of the O 1s features as a function of water exposure is shown in Figure 1c for both CeO$_2$ (black) and CeO$_{2-x}$ (red). It is seen that exposures of less than 2 L are sufficient to saturate the OH/H$_2$O signal and generate ice contributions on the CeO$_2$ and CeO$_{2-x}$ surfaces. Unlike on CeO$_2$, on reduced ceria the OH/H$_2$O component shifts gradually toward lower BE with increasing water dose. Such shifts could indeed point to the presence of two spectral components in the peak, i.e., OH and chemisorbed H$_2$O.

Evidence for the dissociation of water and formation of OH groups on ceria can be derived from the VB of the two samples. As reviewed by Thiel and Madey$^{1}$ and Henderson,$^7$ molecular water has three occupied states in the VB region assigned to the $\sigma$, $\pi$, and $\sigma$ molecular orbitals. In contrast, surface OH gives rise to only two features that correspond to the $1\pi$ and $3\sigma$ states. The VB spectra obtained from CeO$_2$ and CeO$_{2-x}$ samples are shown in parts d and e of Figure 1, respectively. Note that the presented VBs were acquired with a photon energy of 115 eV, which corresponds to the off-resonance condition and is not sensitive to any resonant features in the VB of ceria.$^{21,35}$ The bottom spectra in both figures show the VB spectra obtained at 300 K from the as-prepared samples, whose principal features were discussed earlier by Mullins et al.$^{34}$ The authors assigned two broad features at 4.5 and 6.5 eV to the O 2p orbitals hybridized with the Ce 4f and 5d orbitals, respectively. Additional spectral features emerge in the VBs of both samples, CeO$_2$ and CeO$_{2-x}$, upon cooling to 160 K and subsequent adsorption of water. On CeO$_2$ (Figure 1d), three features develop at 6.5, 9.3, and 12.5 eV that correspond to the $1\sigma$, $3\sigma$, and $1\pi$ states of molecular water. Our DF calculations also reveal two VB peaks for adsorbed OH groups and three peaks for adsorbed water molecules, which are split similarly to the experimental features. The calculated splittings between the corresponding electronic bands $1\pi$–$3\sigma$ and $3\sigma$–$1\pi$ for the H$_2$O/CeO$_2$ models are 1.8 and 3.8 eV, respectively, in line with the splittings between the experimental peaks.

On CeO$_{2-x}$ (Figure 1e), the corresponding three peaks appear at 6.7, 10.2, and 12.6 eV. The most important difference between the two samples is the clear dominance of only two spectral features at 6.7 and 10.2 eV in the VB of CeO$_{2-x}$ during the initial stage of water adsorption. We assign these peaks to the $1\pi$ and $3\sigma$ states of hydroxyl groups, indicating facile dissociation at low exposure. Above 0.3 L (see Figure 1e), the $3\sigma$/$1\pi$ component develops a small shoulder on the low BE side suggesting the formation of a mixed hydroxyl/molecular water layer on partially reduced ceria.

The influence of water on the oxidation state of ceria can be effectively monitored by RPES, and the fundamentals of the...
method are described elsewhere.\textsuperscript{21,35} Briefly, RPES is based on measuring VB photoemission spectra at photon energies corresponding to the 4d→4f resonance either for the Ce\textsuperscript{3+} or the Ce\textsuperscript{4+} ions. The Ce\textsuperscript{3+} resonance at a photon energy of 121.4 eV is caused by a super-Coster–Kronig decay involving electron emission from the Ce 4f states located about 1.4 eV below the Fermi edge. The Ce\textsuperscript{4+} resonance at photon energy of 124.8 eV involves emission of electrons from O 2p states hybridized with Ce 4f states in the VB around 4.0 eV. Additionally, the VB spectrum at photon energy of 115 eV (off-resonance) is measured. Resonant enhancements for Ce\textsuperscript{3+}, D(Ce\textsuperscript{3+}) and for Ce\textsuperscript{4+}, D(Ce\textsuperscript{4+}) are quantified by calculating the intensity difference between the corresponding features in- and off-resonance. The amplitudes of D(Ce\textsuperscript{3+}) and D(Ce\textsuperscript{4+}) are directly proportional to the concentrations of Ce\textsuperscript{3+} and Ce\textsuperscript{4+} ions in the sample, respectively.

The development of D(Ce\textsuperscript{3+}) and D(Ce\textsuperscript{4+}) during adsorption of water on CeO\textsubscript{2} (black) and CeO\textsubscript{2−x} (red) is shown in Figure 1f. It is seen that, upon water adsorption on CeO\textsubscript{2}, D(Ce\textsuperscript{3+}) slightly increases. On CeO\textsubscript{2−x}, an initial increase of D(Ce\textsuperscript{3+}) after cooling (see dashed line) and adsorption of 0.1 L of water is followed by a decrease. At the same time, D(Ce\textsuperscript{4+}) on both samples is attenuated by the adsorbed water in a similar manner. The origin of the observed increase of D(Ce\textsuperscript{3+}) as a result of the interaction with water is not clear. Simple dissociation of water into OH\textsuperscript{−} and H\textsuperscript{+} should not change the oxidation state of ceria.\textsuperscript{1,2} The observed effect could be explained in terms of a strong attractive interaction between the water molecule and subsurface or bulk oxygen vacancies\textsuperscript{5,6} or by a change of the electronic configuration of the Ce\textsuperscript{3+} ion as a result of the interaction with the OH group.\textsuperscript{12} According to our observations, the change of the electronic structure on partially reduced ceria is directly related to the formation of OH groups and, therefore, may indicate water dissociation. A slighter reduction of stoichiometric CeO\textsubscript{2} could
thus be explained by dissociation of a small fraction of water at defects or steps (see Section 3.2.2).

3.2. Desorption and Dissociation of Water during Annealing on Stoichiometric CeO$_2$(111) and Partially Reduced CeO$_2$-x. 3.2.1. Identification of Adsorbed Species. The development of the O 1s spectra during annealing of CeO$_2$(111) and CeO$_2$-x pre-exposed to water at 160 K is shown in parts a and b of Figure 2, respectively. It is seen that the peaks associated with ice on CeO$_2$ (532.9 eV) and CeO$_{2-x}$ (533.5 eV) gradually decrease until they vanish on both samples at 275 K. The peaks associated with OH/H$_2$O on CeO$_2$ (530.9 eV) and CeO$_{2-x}$ (532.0 eV) gradually decrease while the peaks associated with lattice oxygen, O$^2-$ (Ce$^{4+}$) increase. The evolution of the integrated intensities of the peaks in the O 1s spectra obtained from CeO$_2$ (black) and CeO$_{2-x}$ (red) as a function of temperature is shown in Figure 2c. Note that the OH/H$_2$O peak contains a small contribution from O$^2-$ near Ce$^{3+}$ ions on CeO$_{2-x}$, which is not resolved in Figure 2a but subtracted from the integrated intensities in Figure 2c. The figure demonstrates that the thermal stability of the OH/H$_2$O surface species differs for the two samples. The signals from OH/H$_2$O species disappear at 400 K for CeO$_2$, and at 500 K for CeO$_{2-x}$ (see Figure 2c). Unlike on CeO$_2$, the intensity of OH/H$_2$O is almost constant up to 350 K on CeO$_{2-x}$. Another difference between the two samples is the effect of annealing on the BE of the OH/H$_2$O peak. Its position does not change on CeO$_2$, whereas it shifts to higher BE on CeO$_{2-x}$ (compare parts a and b of Figure 2). In Figure 2d, the separation between the BEs of the lattice oxygen (O$^2-$ (Ce$^{4+}$)) and OH/H$_2$O is plotted as a function of temperature for both samples. It is seen that annealing has little effect on the BE separation between the two peaks on CeO$_2$. In contrast, the peak separation increases by $\sim 0.5$ eV upon annealing of CeO$_{2-x}$ to 350 K.

The development of the VB during annealing of CeO$_2$(111) and CeO$_{2-x}$ after exposure to water at 160 K and subsequent annealing is shown in parts e and f of Figure 2, respectively. As discussed above, three peaks at 6.5, 9.3, and 12.5 eV corresponding to the 1b$_1$, 3a$_1$, and 1b$_2$ states of molecular water are resolved on CeO$_2$(111). We observe that the intensities of all three features decrease gradually upon annealing. Above 200 K, the 1b$_1$ state completely disappears whereas two weak features at 6.5 and 9.3 eV can be traced in the spectra up to 400 K (see Figure 2e). Similarly to stoichiometric CeO$_2$, the 1b$_2$ state also disappears from the VB of CeO$_{2-x}$ above 200 K. However, two strong bands at 6.7 and 10.2 eV remain visible until 500 K on CeO$_{2-x}$, indicating high thermal stability of hydroxyl groups on partially reduced CeO$_{2-x}$.

In Figure 2g, the evolution of the D(Ce$^{3+}$) and D(Ce$^{4+}$) resonances for CeO$_2$(111) (black) and CeO$_{2-x}$ (red) is plotted as a function of temperature. On CeO$_2$, D(Ce$^{3+}$) decreases, and D(Ce$^{4+}$) increases to values similar to the as-prepared sample at about 350 K. This behavior is consistent with decomposition/desorption of the OH group in this temperature range. The growth of D(Ce$^{3+}$) on CeO$_{2-x}$ indicates increasing dissociation of water and formation of hydroxyl groups with increasing temperature. D(Ce$^{3+}$) reaches a maximum at about 380 K; note that the BE separation between O$^2-$ (Ce$^{4+}$) and OH/H$_2$O (see Figure 2d) peaks reaches a maximum at the same temperature. The gradual increase of D(Ce$^{4+}$) is consistent with desorption/decomposition of water/hydroxyl on both samples.

It appears that the majority of hydroxyl groups are formed immediately upon adsorption of water at 160 K, on both CeO$_2$(111) and partially reduced CeO$_{2-x}$. Since hardly any change in D(Ce$^{3+}$) is observed upon annealing of CeO$_2$(111) we conclude that practically all defect sites active for water dissociation react upon adsorption at low temperature. The amount of hydroxyl groups formed on CeO$_2$(111) is, however, insufficient to contribute significantly to either the intensity or the BE of the OH/H$_2$O component. Contrary to this, hydroxyl groups are the principal species on CeO$_{2-x}$. An increase in D(Ce$^{3+}$) and BE separation indicated a further increase in the concentration of hydroxyl groups during annealing.

In summary, three characteristic experimental indications of water dissociation and formation of hydroxyl groups are identified in the O 1s spectra, VB spectra, and RPES on CeO$_2$(111) and partially reduced CeO$_{2-x}$. (i) the presence of 1$\pi$ and 3$\sigma$ states in the VB; (ii) the increase of the BE separation between the lattice oxygen, O$^2-$ (Ce$^{4+}$), and OH/H$_2$O; (iii) the increase of D(Ce$^{3+}$) resonance.

3.2.2. IRAS and DFT Studies: Geometry of Water and OH on Ceria. The IR absorption spectra obtained from CeO$_2$ and CeO$_{2-x}$ after exposure to 24 L of D$_2$O at 110 K are shown in parts a and b of Figure 3. Two bands emerge in the spectral regions of the OH$^-$ stretch and OD$^-$ bend OD within multilayer water (ice).$^{36,37}$ The band at 2730 cm$^{-1}$ is associated with dangling OD groups of water molecules in 3D ice islands.$^{38-40}$

Surprisingly, the bands at 2525 and 2730 cm$^{-1}$ disappear after annealing to 200 K on both samples. In view of the O 1s spectra described in section 3.2.1, a substantial amount of surface species, either in the form of chemisorbed water or hydroxyl groups, should be left on the surfaces of both samples, CeO$_2$ and CeO$_{2-x}$, under these conditions. Only the multilayer water (ice) layer should have desorbed (see parts a–c of Figure 2). However, the remaining species are apparently not detectable in the IRAS experiment. We attribute the remarkable insensitivity of IRAS experiment to surface OD/D$_2$O to an unfavorable inclined geometry and small dynamic dipole moment of the surface species on ceria leading to a very low relative absorption signal.$^{30-42}$

The configuration of water molecules on extended CeO$_2$(111) surfaces has been extensively modeled by DFT methods.$^{5-7}$ Since CeO$_2$(111) films prepared on Cu(111) are rather rough$^{19,20}$, we performed a complementary DFT GGA+U study (see section 2.3 for details) of water adsorption on stepped CeO$_2$(111) surface. A slab consisting of two O–Ce–O trilayers with a stripe of a single O–Ce–O trilayer atop$^{52}$ was used to represent a step edge running along the (21T) direction on the (111) surface plane (see Figure 4a; the other panels of Figure 4 display the structures of all studied adsorption complexes b–m). The adsorption of water, estimated by the adsorption energy, $E_{ad}(\text{H}_2\text{O})$, at the terrace, site b, and at the step, site c, is exothermic, suggesting that both sites can be populated upon water adsorption. For site b we obtained $E_{ad}(\text{H}_2\text{O}) = -0.50$ eV, very close to the values of $-0.52$ and $-0.49$ eV reported by Marrocchelli and Yildiz$^{43}$ and by Fronzi et al.$^{45}$ At the step site c the water molecule is more strongly bound by 0.39 eV, with $E_{ad}(\text{H}_2\text{O}) = -0.89$ eV.

In both these cases, the water molecules are strongly tilted with respect to the surface normal. This adsorption geometry will decrease the perpendicular component of the dynamic dipole moment of the O–D stretching mode in the limit of low coverage. Note that the metal surface selection rule (MSSR) requires a component of the dynamic dipole moment normal to

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the surface in a vibrational mode for the detection of the respective IR peak. The MSSR also holds for both CeO$_2$(111)/Cu(111) and CeO$_2$–/Cu(111) systems because the thicknesses of the oxide films are much smaller than the IR wavelengths. We assume that at higher coverage building of water clusters will result in hydrogen bond formation which strongly broadens and, therefore, obscures the O$ -$D bands.

In addition to molecular adsorption, we also considered heterolytic dissociation of H$_2$O at terraces, sites d and e, and step edges, sites f–h, on stoichiometric CeO$_2$(111). We found that water dissociation from the gas phase at the terrace sites depends strongly on the type of formed surface hydroxyl groups, from endothermic, $0.64$ eV (site d), to slightly exothermic, $-0.29$ eV (site e). However, with respect to the adsorbed water molecule, the process on site e is endothermic by $0.21$ eV in agreement with Fronzi et al. In contrast, the dissociation at these steps becomes favorable with respect to both the gas phase, $-1.21$ and $-1.14$ eV, and adsorbed H$_2$O molecules, $-0.32$ and $-0.25$ eV, for configurations f and g, respectively. In the most stable configuration f, the released proton forms an OH group with 2-fold coordinated oxygen, while the OH$ -$ remains coordinated to one of the Ce$^{4+}$ ions. The O–H vibrational frequency of the 2-fold OH group, 3762 cm$^{-1}$ (2736 cm$^{-1}$; here and in the following the corresponding calculated O$ -$D stretching frequencies are given in italics), is close to that of the isolated one i, while the frequency of the 1-fold group is calculated to be about 50 cm$^{-1}$ higher.

According to Fronzi et al., formation of hydroxyl groups from water on reduced CeO$_2$– can be modeled as adsorption of hydrogen atoms on stoichiometric ceria. This assumption has been validated experimentally by Gritschneder and Reichling, who observed that OH$ -$ groups occupy the exact positions of the missing lattice oxygen. In each of our models, shown in Figure 4, configurations i–m, the hydroxyl group was produced by attachment of a single H atom at the corresponding surface O center; concomitantly, one of the surface Ce$^{4+}$ ions in proximity of the OH group is reduced to Ce$^{3+}$ (labeled in blue in Figure 4). This is similar to the
experimental conditions for water dissociation at the CeO$_{2-x}$ sample since the formation of hydroxyl groups by dissociation of H$_2$O on it does not cause reoxidation of Ce$^{3+}$ to Ce$^{4+}$, as discussed in sections 3.1 and 3.2.1. Attachment of H to a 3-fold O center in the configurations l and m provides stabilization (computed with respect to $\frac{1}{2}$ H$_2$) by −0.76 and −0.70 eV, respectively. The corresponding terrace OH groups do not form hydrogen bonds with nearest oxygen ions. On the contrary, the 3-fold OH groups in the proximity of the step form weak hydrogen bonds with nearest oxygen ions, configurations j and k, which are stabilized by −0.89 eV. Thus, one can estimate the energy of these hydrogen bonds to be 0.1−0.2 eV.

The hydroxyl group at the 2-fold coordinated oxygen at the step, site i, stabilized by −1.21 eV, is found to be the most favorable energetically. It suggests preferential formation of the 2-fold hydroxyls over the 3-fold ones. According to our calculations, the OH axis of the 2-fold hydroxyl group is tilted by 70° away from the surface normal. Such an arrangement of a hydroxyl group on reduced CeO$_{2-x}$ or stoichiometric CeO$_2$(111) surfaces (in addition to its inherently small dynamic dipole moment) explains the missing O−D stretching bands in IRAS above 200 K. Indeed, the calculated IR intensity of the O−H vibration even for structure l, where the OH group is perpendicular to the CeO$_2$(111) surface, is small. For instance, it is about 40 times smaller than the intensity of the C−O stretching mode of a CO molecule adsorbed on Pt(111). The energetically favorable inclination of the OH group from the surface normal (such as in structure i) further reduces the small IR intensity of OH group. Note that calculated stretching O−H (O−D) vibrational frequencies for both 2- and 3-fold hydroxyl groups are within the narrow range of 3763−3777 (2737−2747) cm$^{-1}$. The difference in the O−H stretching frequencies between species d−m in the range of

Figure 5. O 1s core level (a) and VB (d) spectra during annealing of Pt/CeO$_2$(111) exposed to the total doses of 10 L of H$_2$O at 160 K. The O 1s (a) and the VB (d) spectra were acquired with photon energies of 650 and 115 eV, respectively. Integrated intensities of O 1s spectral components (b), BE separation between O$^2$−(Ce$^{4+}$) and OH/H$_2$O components (c), and D(Ce$^{3+}$) and D(Ce$^{4+}$) resonant enhancement (e) as functions of temperature.
70–140 cm$^{-1}$ is caused by formation of weak hydrogen bonds (the frequency shift may be overestimated in the calculations, in particular for stronger hydrogen bonds$^{45}$). The only case with strong hydrogen bond, characterized by the bond distance 153 pm and stretching frequency 2606 (1908) cm$^{-1}$, is found for water dissociation on the terrace (structure e), which is, however, energetically disfavored with respect to the non-dissociative adsorption (structure b).

### 3.3. Dissociation of Water on Pt/CeO$_2$

In the final step we investigated the interaction of water with Pt nanoparticles supported on CeO$_2$(111) films$^{22,29}$. The O 1s spectra obtained from Pt/CeO$_2$ exposed to a total dose of 10 L of H$_2$O at 160 K and subsequently annealed stepwise to 500 K are plotted in Figure 5a.

As discussed in section 3.1, the O 1s spectrum at 160 K contains spectral contributions from lattice oxygen in ceria, (O$^{2-}$(Ce$^{4+}$)), at 529.5 eV, the multilayer water (ice) at 533.0 eV, and unresolved contributions from OH and chemisorbed H$_2$O, OH/H$_2$O, at 531.1 eV. Because of the large width of the peaks at 533.0 and 531.1 eV, however, the corresponding species adsorbed on ceria and those on Pt particles cannot be resolved. Therefore, the intensity of the components shown in Figure 5b contains contributions from the species on both ceria and Pt particles. Since deposition of Pt on stoichiometric CeO$_2$(111) gives rise to immediate formation of a small fraction of Ce$^{4+}$ ions,$^{29}$ the contribution from O$^{2-}$(Ce$^{4+}$) to the intensity of the peak at 531.1 eV should not be ignored. The BE separation between O$^{2-}$(Ce$^{4+}$) and OH/H$_2$O is shown in Figure 5c.

The VB spectra obtained from Pt/CeO$_2$ exposed to a total dose of 10 L of water at 160 K and subsequently annealed stepwise to 500 K are shown in Figure 5d. The VB at 160 K contains contributions from water, molecularly adsorbed on both ceria and Pt particles. The red and green lines in the VB indicate the positions of the VB features of water on both ceria and Pt particles. Note that the peak at 531.1 eV should not be ignored. The BE separation between O$^{2-}$(Ce$^{4+}$) and OH/H$_2$O is shown in Figure 5e.

The VB spectra obtained from Pt/CeO$_2$ exposed to a total dose of 10 L of water at 160 K and subsequently annealed stepwise to 500 K are shown in Figure 5d. The VB at 160 K contains contributions from water, molecularly adsorbed on both ceria and Pt particles. The red and green lines in the VB indicate the positions of the VB features of water on both ceria and Pt particles. Note that the peak at 531.1 eV should not be ignored. The BE separation between O$^{2-}$(Ce$^{4+}$) and OH/H$_2$O is shown in Figure 5c.

According to the literature$^{13,15,46-50}$ water does not dissociate on Pt(111) or stepped Pt(111) surfaces. Note that Pt/CeO$_2$ was flashed only to 500 K prior to water adsorption. Annealing to higher temperature will lead to stronger reverse oxygen spillover from ceria to Pt.$^{29}$ Even if a small amount of oxygen reverse spillover occurred, the resulting oxygen coverage on the Pt particles would be extremely small.$^{29,22}$ This is important as spilt-oxygen could, in turn, trigger dissociation of water.$^{13-15}$ Since we did not observe any increase of D(Ce$^{3+}$) (data not shown) during the adsorption of water, we assume that the principal species on the surface of Pt/CeO$_2$ at 160 K are chemisorbed water and ice.

During annealing to 500 K (see Figure 5b), the intensity of the peak at 533.0 eV (ice) gradually decreases while that at 529.5 eV (O$^{2-}$(Ce$^{4+}$)) increases. The intensity change of both peaks is caused by desorption of water. In parallel, the intensity of the feature at 531.1 eV (OH/H$_2$O) decreases above 350 K, while its BE gradually shifts to higher values (see Figure 5a). The BE separation between the peaks associated with OH/H$_2$O and O$^{2-}$(Ce$^{4+}$) reaches the highest values between 250 and 350 K before it decreases again above 350 K. In parallel, we observe a substantial increase of D(Ce$^{3+}$) above 180 K (see Figure 5e), reaching a maximum at about 250 K, and then decreasing to a value similar to that of the as-prepared sample.

In view of the discussion in the previous sections, the observed behavior suggests that the majority of hydroxyl groups formed during annealing to 350 K are located on ceria rather than on Pt: if most of the hydroxyl groups were formed on Pt the BE separation between the OH/H$_2$O and O$^{2-}$(Ce$^{4+}$) peaks would decrease rather than increase.$^{13}$

A possible pathway for the formation of hydroxyl groups on ceria involves the dissociation of water on the surface of the Pt particle or at the Pt/ceria interface followed by spillover of hydrogen to the support. Earlier we observed a similar reduction and reoxidation of ceria during annealing of Pt/CeO$_2$ upon exposure to hydrogen at low temperature and subsequent annealing.$^{32}$ The production of hydroxyl species was suggested to be formed by spillover of hydrogen and were shown to be stable up to 260 K.$^{35}$

The unequal amounts of the OH groups on Pt and CeO$_2$ suggest a rather complex chemistry. Simple dissociation of water into OH and H on Pt followed by hydrogen spillover to CeO$_2$ would yield equal amounts of OH groups on both Pt and CeO$_2$. There must be additional processes that may lead to an increase of hydroxyl groups on ceria. Such processes may involve (1) dissociation of OH to oxygen and hydrogen on Pt followed by spillover of hydrogen to ceria; (2) spillover of OH groups from Pt to ceria; (3) OH recombination on Pt to oxygen and water followed by desorption or subsequent dissociation of water. According to Grabow et al.,$^{31}$ processes 1 and 2 involve high activation barriers and therefore are very unlikely to occur under our experimental conditions. In contrast, the OH recombination occurs almost spontaneously and may fully account for the reduced concentration of OH groups on Pt.$^{31}$

In view of the lack of sensitivity of the IRAS experiment to low coverages of surface OH groups (see section 3.2) it is not surprising that these species are not observed in IRAS. The corresponding spectra obtained from Pt/CeO$_2$ after adsorption of 50 L of D$_2$ at 150 K followed by annealing to 240 and 320 K are shown in Figure 3c. Upon deuterium spillover from Pt to ceria, an OD band should appear around 2700 cm$^{-1}$; however, the spectrum remains featureless after annealing to 240 and 320 K. As SRPES and RPES provide clear proof of spillover, we attribute the lack of sensitivity of the IRAS experiment to the low dynamic dipole moment and the strongly tilted and hydrogen bond nature of the hydroxyl groups formed. Note that vibrational bands for dissociatively adsorbed D$_2$ on Pt$^{46}$ (as on other metals$^{33-35}$) appear at low frequency and are not accessible in the present experiment.

The decrease of D(Ce$^{3+}$) above 260 K (see Figure 5e) is consistent with the decomposition of OH groups on ceria and reverse spillover of hydrogen from ceria to Pt. As discussed in detail in our previous work,$^{35}$ hydrogen spillover becomes reversible in this temperature region. Therefore it may recombine with OH groups or atomic oxygen left on Pt and desorb as water. After complete water removal at 500 K the peak at 529.5 eV (O$^{2-}$(Ce$^{4+}$)) had intensity similar to that of before adsorption of water. The small shoulder left in the O 1s spectrum at 500 K (see Figure 5a) corresponds to the small amount of O$^{2-}$(Ce$^{4+}$) also present on the as-prepared sample.

### 4. CONCLUSIONS

We investigated the chemistry of water on well-ordered stoichiometric CeO$_2$(111), partially reduced CeO$_2$-$\delta$, and Pt/CeO$_2$ combining SRPES, RPES, IRAS, and DF calculations.
We have found that adsorption of H$_2$O at 160 K is mostly molecular on CeO$_2$(111) and partially dissociative on CeO$_2$-x. Formation of hydroxyl (OH) groups has been observed during adsorption and annealing on both samples. We find three typical characteristics that can be used to identify OH groups on ceria: (i) the presence of 1$s$ and 3$s$ states in VB; (ii) the increase of the BE separation between the O 1s spectral components of lattice oxygen, O$^{2-}$ (Ce$^{4+}$), and OH/H$_2$O; (iii) the increase of D(Ce$^{3+}$) resonance.

The results of DF calculations show that the energetically most favorable surface species on stoichiometric CeO$_2$ terraces is adsorbed water, while dissociation is disfavored by about 0.2 eV. At the steps, the adsorption energy of water is higher than on the terraces but there dissociation of water was found to dominate the molecular adsorption.

Dissociation of water and formation of OH groups readily takes place on partially reduced CeO$_2$-x. Hydroxyl groups at 2-fold oxygen sites (with respect to cerium ions) were calculated to be more stable than those at 3-fold oxygen sites. However, all favorable configurations of chemisorbed H$_2$O and OH exhibit strong tilting away from the surface normal on both types of calculated systems (without or with Ce$^{4+}$ ions) that model CeO$_2$(111) and CeO$_2$-x samples. This adsorption geometry, in combination with the small dynamic dipole moment of the OH stretch, makes it extremely difficult to detect these species in IRAS, and explains the featureless IR spectra above 200 K, i.e., combination with the small dynamic dipole moment of the OH.

The interaction of water with CeO$_2$-x does not cause any detectable reoxidation of Ce$^{3+}$ into Ce$^{4+}$. The dissociation of water is fully reversible, yielding either molecular water (recombination of OH groups) or release of hydrogen and oxygen into the gas phase. The oxidation state of CeO$_2$-x after desorption/decomposition of H$_2$O/OH is fully recovered to that before water adsorption.

Adsorption of water on Pt/CeO$_2$ is molecular at 160 K. We find partial dissociation of water, either on Pt or at Pt/ceria interface, followed by spillover of hydrogen to the support in the temperature interval between 180 and 250 K. This leads to formation of hydroxyl groups on ceria in this temperature region. Above 250 K, decomposition of hydroxyl groups on ceria and reverse spillover of hydrogen to Pt occurs, followed by desorption of molecular water. Whereas initial spillover of hydrogen leads to a significant alteration of the oxidation state of cerium, reverse-spillover of hydrogen and subsequent desorption of water up to 300 K fully restores the oxidation state of ceria on the Pt/CeO$_2$ model catalyst.

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