The Surface Chemistry of Cerium Oxide

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Abstract

This review covers the structure of, and chemical reactions on, well-defined cerium oxide surfaces. Ceria, or mixed oxides containing ceria, are critical components in automotive three-way catalysts due to their well-known oxygen storage capacity. Ceria is also emerging as an important material in a number of other catalytic processes, particularly those involving organic oxygenates and the water-gas shift reaction. Ceria's acid-base properties, and thus its catalytic behavior, are closely related to its surface structure where different oxygen anion and cerium cation environments are present on the low-index structural faces. The actual structure of these various faces has been the focus of a number of theoretical and experimental investigations. Ceria is also easily reducible from CeO_2 to CeO_{2-x} . The presence of oxygen vacancies on the surface often dramatically alters the adsorption and subsequent reactions of various adsorbates, either on a clean surface or on metal particles supported on the surface. Most surface science studies have been conducted on the surfaces of thin-films rather than on the surfaces of bulk single crystal oxides. The growth, characterization and properties of these thin-films are also examined.

List of abbreviations

AP-XPS	Ambient pressure x-ray photoelectron spectroscopy
AR-MSRI	Angle resolved mass spectrometry of recoiled ions
DFT	Density functional theory
DRS	Direct recoil spectroscopy
FTIR	Fourier transform infrared spectroscopy
GGA	Generalized gradient approximation
HREELS	High resolution electron energy loss spectroscopy
LEED	Low energy electron diffraction
LEEM	Low energy electron microscopy
LEIS	Low energy ion scattering
LCVD	Laser chemical vapor deposition
MOCVD	Metalorganic chemical vapor deposition
NC-AFM	Non-contact atomic force microscopy
NC-SFM	Non-contact scanning force microscopy
NEXAFS	Near-edge x-ray absorption fine structure
PEEM	Photoemission electron microscopy
PLD	Pulsed laser deposition
RAIRS	Reflection – absorption infrared spectroscopy
RBS	Rutherford back scattering
RER	Resonant enhancement ratio
RHEED	Reflection high energy electron diffraction
RPES	Resonant photoelectron spectroscopy
SMSI	Strong metal support interaction
STM	Scanning tunneling microscopy
sXPS	Soft x-ray photoelectron spectroscopy
TDS	Thermal desorption spectroscopy
TPD	Temperature programmed desorption
WGS	Water-gas shift reaction
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
YSZ	Yttria-stabilized zirconia

1 – Introduction

The fundamental interest in and commercial applications of cerium oxide as a catalytic material have accelerated rapidly in recent years. This progression has been tracked from the seminal review article by Alessandro Trovarelli in 1996[1] through two subsequent books in 2002[2] and 2013[3]. In the most recent volume Delgado et al identified many catalytic applications of ceria-based materials.[4] These include pollution abatement, steam and dry reforming of hydrocarbons and oxygenates, CO oxidation and preferential CO oxidation in the presence of H₂ (PROX), water-gas shift (WGS), conversion of syngas to alcohols, C-C coupling, aldol condensations, partial oxidation and selective hydrogenation. Organic syntheses catalyzed by ceria that involve more complex reactants and products have been reviewed by Vivier and Duprez.[5] Of these various applications the use of ceria, or mixed oxides containing ceria, in automotive three-way catalysts (TWC) has been the most widespread and technologically successful.[4]

In a classic overview of organic reactions on metal oxide surfaces, Barteau identified three key concepts for understanding the surface chemistry of metal oxides.[6] These are: (1) the coordination environment of the surface atoms; (2) the redox properties of the oxide; and (3) the oxidation state of the surface. With respect to these three concepts cerium oxide is an ideal material for testing and understanding the influence of these characteristics. As will be discussed below, as a cubic material cerium oxide has a relatively simple structure. However each of its stable, low-index crystallographic faces exposes Ce cations and O anions with different numbers of coordination vacancies. Ceria is easily reducible, as evidenced by its use as an oxygen storage material in three way catalysts. Calculations have indicated that the oxygen vacancy formation energy, which is related to the reducibility, is approximately 30% lower on ceria surfaces compared to bulk.[7-9] This suggests that reactions that involve the exchange of O between adsorbates and the surface may occur readily on ceria surfaces. Further, these calculations indicate that the O-vacancy formation energy will vary from face to face. Therefore oxidation and reduction reactions are likely to be different on the different faces. Finally, when O vacancies are created, two of the Ce cations adjacent to the vacancy change from Ce⁴⁺ to Ce³⁺. As will be shown, adsorption and reaction on reduced ceria surfaces may differ dramatically from the chemistry of the same adsorbate on a fully oxidized CeO₂ surface.

It has been frequently demonstrated that the “surface science approach”, i.e. experiments on a well characterized, single crystal surface in an ultrahigh vacuum environment, has been invaluable for understanding the fundamental interactions between adsorbates and surfaces. However, surface science studies on cerium oxide have only recently been coming

into their own. As noted in one of the first reviews of the surface science of ceria, up to 1998 there were only a handful of references related to surface science studies on ceria.[10] While the number of papers has been growing, there have been no comprehensive reviews in the past decade. We note that several more limited reviews have included ceria within an overview of the chemistry on a number of oxides.[11,12]

Computational studies on ceria had been limited by the inability of traditional DFT methods to adequately describe adsorption and reaction on metal oxides containing unoccupied f-orbitals. Recent advances have largely overcome this barrier and there are several excellent reviews covering computational studies on ceria.[9,13]

Following a brief description of the experimental and computational methods that have been used to study the chemistry on ceria (Section 2), the structural properties of $\text{CeO}_2(111)$, $\text{CeO}_2(110)$ and $\text{CeO}_2(100)$ will be discussed in detail (Section 3) since they are critical for understanding the chemical behavior of these surfaces. Most experimental studies on ceria surfaces have been conducted on cerium oxide thin films deposited on other substrates. There have been a number of different deposition methods and substrates and these will be discussed in Section 4. The two largest sections of this review will cover adsorption of various molecules on clean ceria surfaces (Section 5) and on metals supported on ceria surfaces (Section 6). Section 6 will begin with an overview of the characterization of different metals on ceria in the absence of adsorbates.

2 – Experimental Methods

The methods used to study adsorption and reaction on cerium oxide surfaces can be grouped into four general areas; structural characterization, spectroscopic techniques, reaction analysis, and theoretical / computational methods. Structure / function relationships are inherently important for understanding the reaction behavior on ceria surfaces. Therefore it is essential to characterize the structure of the various ceria surfaces that are examined. In certain instances it is also possible to ascertain by microscopy or spectroscopy the adsorption site and/or orientation of adsorbed species on the surface. Spectroscopic techniques are primarily used to identify adsorbed species and to determine the oxidation state of the Ce in the substrate. Analysis of products that leave the surface directly relates to the catalytic properties of the substrate. Computational methods have been used to determine the structure and properties of the clean surfaces, the stability, nature and adsorption sites of adsorbates on the surface, and the reaction pathways from gas phase reactants through adsorbed intermediates to desorbed products.

2.1 – Structural Characterization

Although it's primarily a bulk characterization technique, x-ray diffraction (XRD) has been used to study cerium oxide thin films. Polar and azimuthal scans have demonstrated that films grown on single crystal substrates are predominantly single crystal with their surface normal aligned to expose a specific low-index crystal plane and their azimuths aligned along a specific direction with respect to the single crystal substrate.[14,15] Rutherford backscattering (RBS) has also been used to ascertain the quality of single crystalline films. [14]

Reflection high-energy electron diffraction (RHEED) provides more surface-specific information. [14] The nature of the diffraction pattern, i.e. spots vs. streaks, provides an indication of the roughness of the surface. The azimuthal dependence of the diffraction pattern confirms that the surface lattice is aligned in a manner consistent with the bulk orientation revealed by XRD.

Low-energy electron diffraction (LEED) produces an indication of the order and symmetry of the atoms on the surface. In principle more sophisticated methods such as spot profile analysis (SPA) LEED or LEED-IV could be applied to obtain a more precise determination of structure, relaxation and disorder but these have not been applied to cerium oxide surfaces. Low-energy electron microscopy (LEEM) and photoemission electron microscopy (PEEM) provide video images of surface structure during the growth of ceria films at nanometer resolution.[16] Application of LEED can be hampered by the insulating nature of the substrate that can cause charging and disrupt the low-energy electrons' flight. This can be overcome by using higher energy incident beams[14], reducing the ceria slightly to improve conductivity[17] or studying thin films on conducting substrates.

Several atomic scattering techniques have been used to study ceria surfaces. Direct recoil spectroscopy (DRS) [14], angle resolved mass spectrometry of recoiled ions (AR-MSRI)[18] and low-energy alkali ion scattering (LEIS)[19,20] provide highly surface sensitive information regarding surface structure and composition. Angular variations resulting from shadowing and blocking effects of surface atoms can be modeled for different surface structures and compared to experimental results. Charging does not affect the results in these methods due to either collecting both charged species and neutrals in DRS and AR-MSRI or due to the low neutralization probability of scattered alkali ions.

All of these methods provide area-averaged indications of the surface structure. Scanning probe microscopy produces atomic scale, local information regarding surface structure. Scanning tunneling microscopy (STM) has been performed on the (111)[17], (100)[21]

and (110)[22] faces of bulk cerium oxide. The very low conductivity of stoichiometric CeO_2 necessitated performing these experiments at either elevated temperatures, very low tunneling current or at a very small degree of reduction, $\text{CeO}_{1.99}$ (111). An alternative approach for imaging insulating, bulk CeO_2 (111) surfaces at lower temperatures was to use non-contact atomic force microscopy (NC-AFM)[23-25] / scanning force microscopy (NC-SFM)[26-29]. The low conductivity problem in applying STM to stoichiometric CeO_2 can also be overcome by studying thin films of ceria supported on a conducting substrate. This approach has been widely applied.[30-37].

2.2 – Spectroscopic Methods

One of the most important characteristics of cerium oxide is the oxidation state of the Ce cation. The most commonly used method for determining the Ce oxidation state is measurement of the Ce 3d core level by x-ray photoelectron spectroscopy (XPS).[38-43] As shown in Figure 1 the Ce 3d XPS spectra are complex. The spectra for fully oxidized CeO_2 (111) / Ce^{4+} and fully reduced Ce(III) oxide / Ce^{3+} contain six and four peaks, respectively, rather than two each due to spin-orbit splitting as might be expected for the 3d core-level. The peaks labeled V''' and U''' are associated with the $\text{Ce } 3d^9 \text{ O } 2p^6 \text{ Ce } 4f^0$ final state with a spin-orbit splitting of 16.5 eV. The additional peaks result from so-called “shake-down” states where electrons are transferred from the O 2p level to the Ce 4f level in the excited state. [44,45] A quantitative estimate of the degree of reduction can be obtained from fitting a linear combination of the spectra from the reference materials as shown by the dotted line in Figure 1. This fit indicates that the partially reduced material is 30% Ce^{3+} or $\text{CeO}_{1.85}$. Although the fit in Figure 1 looks reasonable it has been suggested that the relative intensities of the peaks do not remain constant if the ceria is partially reduced.[40] If the line shapes and intensities are not constant the spectrum would need to be fit with ten peaks to determine the relative composition of Ce^{4+} and Ce^{3+} .

The Ce 4d core level spectra show a similar dependence on the Ce oxidation state as shown in Figure 2. Although the intensity of these spectra is much smaller than the Ce 3d spectra when using a laboratory Mg $\text{K}\alpha$ or Al $\text{K}\alpha$ excitation source[42], the intensity is much greater when excited with a lower photon energy as might occur using a synchrotron light source.[43] Assignments of the peaks in the Ce 4d spectra are even more complex than those for the Ce 3d spectra because in addition to spin-orbit splitting and shake-down effects, multiplet splitting occurs due to a coupling of an unpaired electron in the Ce 4d final state with an electron in the Ce 4f level.[46,47] Again the highest binding energy peaks, X''' and W''', are associated

with the simplest final state, $\text{Ce } 4d^9 \text{ O } 2p^6 \text{ Ce } 4f^0$. The spin-orbit splitting is much smaller for Ce 4d, 3.3 eV, compared to 16.5 eV for the Ce 3d spectrum. As shown by the dotted line in Figure 2b, a reasonable fit can be obtained in the Ce 4d spectrum for a partially reduced CeO_{2-x} sample from a linear combination of spectra from the reference materials.

A third approach for determining the Ce oxidation state using photoemission is from valence band spectra. Here the analysis should be straight forward since the intensity of the Ce 4f level should give a direct indication of the occupancy of this state and thus the presence of Ce^{3+} . Using standard laboratory excitation such as HeI or HeII the Ce 4f photoemission is not very intense.[38] The intensity of the Ce 4f as well as the O 2p features are resonantly enhanced using photon energies at the Ce 4d ($\text{Ce } N_{IV}$) edge near 120 eV.[48,49] Matolin et al have applied this technique extensively to study the oxidation, reduction and charge transfer on cerium oxide thin films[50-54] and nanoparticles.[55,56] They have called this method resonant photoelectron spectroscopy (RPES). As shown in Figure 3 the maximum intensity for the Ce 4f peak at 1.4 eV binding energy occurs at an excitation of 121.4 eV while the maximum in the hybridized O 2p feature associated with Ce^{4+} near 4 eV binding energy occurs at an excitation energy of 124.8 eV. Matolin et al have defined resonant enhancement factors ($D(\text{Ce}^{4+})$ and $D(\text{Ce}^{3+})$ in Figure 3) which are the differences in the O 2p and Ce 4f peak intensities on and off resonance.[57] The ratio of $D(\text{Ce}^{3+})/D(\text{Ce}^{4+})$ has been called the resonant enhancement ratio (RER) and is proportional to the percentage of Ce^{3+} in the sample. This method is advantageous compared to the measurement of Ce 3d or Ce 4d level spectra in that it has very high count rates enabling rapid data acquisition, it has a large contrast for samples with only a small variation in Ce oxidation state and it is very surface sensitive since the kinetic energy of the valence electrons, ca. 120 eV, is near the minimum in the mean free path curve for electrons in solids.[58] It should also be noted that the intensity of the Ce 4f peak is enhanced at excitation energies above the resonance maximum and therefore could be used to obtain the Ce^{3+} concentration provided suitable reference standards are also measured.[43]

XPS has also been used extensively to study adsorbates on cerium oxide surfaces.[59-66] To a lesser extent valence level photoemission has also been used to study adsorbates on ceria surfaces.[15,67] The use of synchrotron radiation has been termed soft x-ray photoelectron spectroscopy (sXPS). Using synchrotron radiation as an excitation source has many advantages compared to a standard laboratory excitation source. A synchrotron light source has much higher photon flux / brightness compared to a laboratory source. This is typically accomplished without sacrificing photon energy resolution. The excitation energy is also tunable. This enables high surface sensitivity as a lower kinetic energy of the emitted

electron minimizes the electron mean free path. This is particularly evident when studying the O 1s core-level where the photoemission from a monolayer or less of O in an adsorbate has intensity similar to the emission from the O in the CeO_x substrate.[15,68] In addition the photoemission cross section increases exponentially as the excitation energy gets closer to the ionization energy.[69] We have found that the excitation “sweet spot” is ca. 100 eV above the nominal binding energy of the element being studied. This provides a balance between cross section, surface sensitivity and the intense, rapidly rising background that occurs at low photoelectron kinetic energies.

Synchrotron radiation is also used to perform x-ray absorption spectroscopy. X-ray absorption spectroscopy of adsorbed species using soft x-ray excitation is called near-edge x-ray absorption fine structure (NEXAFS).[70] This technique can provide more precise molecular level identification than core level sXPS, for example differentiating formate, (HCOO)⁻, from carbonate, (CO₃)²⁻, [71] or carbonate from CO₂. [72] It can also provide information regarding adsorbate orientation.[72]

Vibrational spectroscopy can be conducted using high resolution electron energy loss spectroscopy (HREELS)[73] and reflection-absorption infrared spectroscopy (RAIRS).[74] The use of HREELS is complicated by the non-conducting nature of the ceria substrate and the intense phonon modes that dominate the spectra which require deconvolution algorithms to remove them from the spectrum. Its application has been limited.[75,76] Infrared spectra provide precise identification of adsorbed species[77] and also information regarding the surface adsorption site.[62,78,79] The sensitivity is enhanced by reflection of the IR beam from a metal surface[80], therefore the technique is more widely applied on thin ceria films supported on metal surfaces. RAIRS also has the advantage that it can be conducted at elevated pressures as opposed to in a vacuum environment generally required for electron spectroscopy. Thus it can be applied under realistic reaction conditions. Recent advances in ambient pressure XPS (AP-XPS) will make core-level photoemission more readily applicable for studying surface reactions at elevated pressures.[81]

2.3 – Reaction Methods

The most common method for determining the reaction products from adsorbates on ceria surfaces is temperature programmed desorption (TPD), also called thermal desorption spectroscopy (TDS).[82] In this technique one or more reactants are adsorbed on a surface and then a linear temperature ramp is applied to the sample while the desorbing, gas phase products are monitored by a mass spectrometer. This method has been widely applied to

studying reactions on cerium oxide surfaces as is evident in later sections of this report. Two potential difficulties in applying TPD to oxide materials are mounting the sample and accurately recording the sample temperature. Support wires and thermocouples cannot be directly spot-welded to oxide substrates. However, if ceria films are grown on metal substrates spot-welding can be used. Mounting CeO₂ single crystals or ceria films grown on oxide supports requires either support on some sort of metallic holder[83] or the use of ceramic cement to attach the sample to support wires.[19] The thermocouple needs to be attached directly to the oxide sample, typically using ceramic cement, as significant temperature gradients can occur between metal supports and the oxide sample.

The reactivity of ceria surfaces can also be monitored under dynamic conditions. In these experiments the sample is constantly exposed to the reactants rather than exposing the surface to only a monolayer of reactants and then evacuating the chamber. The reactant pressure might be either relatively low, $10^{-5} - 10^{-6}$ torr,[84,85] or at elevated pressures greater than 1 torr.[86,87] The products can be monitored either by a mass spectrometer or, in the case of experiments at elevated pressures, a gas chromatograph. Further, the experiments can be conducted at constant temperature and pressure, in which case kinetic parameters can be extracted, or as the sample temperature is ramped.

2.4 – Computational Methods

Two extensive reviews of the computational approaches applied to cerium oxide have been produced by Sauer, et al.[9,13] The earlier paper placed the theoretical work on cerium oxide, a rare earth oxide, in context with similar calculations conducted on transition metal oxides. The latter work focused solely on cerium oxide. As with most computational work applied to solid surfaces and reactants on solid surfaces, the vast majority of theoretical work on cerium oxide has been performed within the framework of density functional theory (DFT). The greatest limitation to the application of standard DFT to cerium oxide has been an accurate description of reduced CeO_{2-x}. The two electrons released to the surface through the removal of neutral $\frac{1}{2}\text{O}_2$ are deposited in the 4f level of cerium. DFT delocalizes these electrons through the Ce in the substrate producing a fractional occupation of the 4f orbital with a metallic ground state.[13] There have been two approaches to correcting the DFT calculations; a) correction of the on-site Coulomb correlation through a Hubbard U-term (known as DFT+U), or b) the use of hybrid functionals which add a fraction of the Fock exchange energy to the DFT exchange energy.[9] The DFT+U approach has been the most widely applied because the use of hybrid functionals is comparatively computationally expensive. One significant limitation of the DFT+U

method noted by Paier, et al is that energy diagrams for catalytic reactions on ceria will be too exothermic when ceria is reduced and too endothermic when ceria is re-oxidized.[9]

3 – Structure

Fully oxidized CeO_2 has the fluorite (CaF_2) crystal structure, space group $Fm3m$. [88] As shown in Figure 4 the Ce cations are arranged in a face-centered cubic structure with the O anions embedded within the unit cell in a simple cubic arrangement. The lattice constant of the cubic unit cell is 0.541 nm. The Ce cations are bonded to eight O nearest neighbors while the O anions are tetrahedrally bonded to four Ce nearest neighbors. Note that although the Ce occupy FCC-like sites they are not close-packed with respect to their Ce nearest neighbors.

The stable form of the fully reduced sesquioxide, Ce_2O_3 , is hexagonal, space group $P3m1$. In this structure the Ce cations are coordinated to seven O anions, with four oxygens closer than the other three. However, it has been well-established that intermediate compositions of CeO_{2-x} with $0.5 < x \leq 0$ have a structure based on a fluorite lattice with the Ce retaining near FCC-like positions and O-vacancies either randomly distributed or ordered depending on composition and temperature.[89-91] The limiting structure for fluorite-based Ce_2O_3 is BCC-type C or bixbyite, space group $Ia3$. This has a very large unit cell with 32 Ce atoms and 48 O atoms. The Ce are coordinated to six O.

In this review we will be considering the low-index faces of CeO_2 , i.e. (111), (110) and (100). These three surfaces are prototypical examples of three types of ionic crystal surfaces whose stability was considered by Tasker.[92] $\text{CeO}_2(110)$ is a Type 1 surface with each layer having zero charge due to a stoichiometric balance of anions and cations in each plane (Figure 5). $\text{CeO}_2(111)$ is a Type 2 surface. Each plane is charged but the repeat unit consists of three planes in a symmetrical configuration resulting in no net dipole moment perpendicular to the surface (Figure 6). Type 1 and Type 2 surfaces should have relatively low surface energies and should produce surfaces with only modest relaxations compared to a bulk truncation. A bulk truncation along $\text{CeO}_2(100)$ creates a Type 3 surface. This surface has alternately charged planes with a repeat unit of only two planes producing a dipole moment perpendicular to the surface (Figure 7a). Such a surface would have a nearly infinite free energy and therefore will require a major reconstruction compared to the bulk. A straight-forward way to eliminate the dipole moment is to remove half of the ions from one layer and move them to the opposing face as shown in Figure 7b. An alternative way of envisioning this structure is that it is similar to a Type 2 structure, i.e. a three-layer repeat unit A-B-A-A-B-A-, except that the interior layers of O are interlaced / co-planar.

There have been many computational studies on the structure and stabilities of these three low-index surfaces of CeO_2 . [7,93-101] While the methods and absolute results may vary, the general consensus is that stability of these three surfaces runs in the order $(111) > (110) > (100)$. The surface energies are stabilized by relaxation with a contraction between the first and second layers. The degree of relaxation runs in the reverse order of the surface energies with the O anions on the surface of $\text{CeO}_2(100)$ contracting the most and those on $\text{CeO}_2(111)$ the least. Calculations on $\text{CeO}_2(110)$ have indicated that the Ce contracts more than the O creating a ripple in the top layer. [95,97] Calculations of $\text{CeO}_2(100)$ have started with a model where half of the O is removed from the top surface and placed on the bottom surface in order to eliminate the dipole normal to the surface. [93,95,97,100] Most have assumed the so-called “checkboard” arrangement of O as shown in Figure 7b. Skorodumova et al tested other arrangements of O and determined that the checkerboard arrangement was the most stable. [95] However the energy difference between different arrangements was small suggesting that deviations from a perfect geometry could easily occur.

Experimental studies of $\text{CeO}_2(111)$ by LEED [17,36,37,102], ion scattering [20] and STM / AFM [17,24-27,34,36,37,103,104] are consistent with the structure shown in Figure 6. Ion scattering established that the surface was terminated by O. [20] This was corroborated by scanning probe microscopy studies where vacancies are observed suggesting that the surface is terminated by O. Figure 8 demonstrates various features on a $\text{CeO}_2(111)$ revealed by scanning force microscopy. [104] Figure 8a shows a relatively wide area image, $(100 \times 100) \text{ nm}^2$. The surface is not perfectly flat but is composed of stacked terraces. This structure has been observed on both a single crystal surface, as in Figure 8a, and on $\text{CeO}_2(111)$ thin films (Figure 9a). A line scan across the terraces, Figure 8b, indicates that each terrace is 0.31 nm tall corresponding to an O-Ce-O tri-layer as shown in the sideview at the bottom of Figure 6. Atomic resolution shown in Figure 8c demonstrates that the surface has the ideal geometry as shown in Figure 8d and Figure 6. Finally the terrace edges are predominantly oriented along (110) and (001) directions creating hexagonal structures (Figure 8i and 8ii) and corners with 120° angles.

Nörenberg and Briggs conducted LEED, RHEED and STM studies on single crystal $\text{CeO}_2(110)$. [22] LEED and RHEED indicated a (2×1) reconstruction. STM showed lines running in the $[11\ 0]$ direction separated by 1.1 nm. Referring to Figure 5 these lines run along the rows of Ce cations. The separation is equal to twice the distance between Ce rows in the $[100]$ direction. Similar STM structures were observed on the structurally isomorphic $\text{UO}_2(110)$ surface. [105] Muggelberg et al ascribed the STM structure to a missing row reconstruction of the $\text{UO}_2(110)$ surface. When the $\text{CeO}_2(110)$ surface was annealed to 1030°C the surface

facetted. RHEED patterns recorded along the $[11\ 0]$ azimuth revealed streaks tilted by 35° . This is the angle between the (110) plane and the (111) and $(\bar{1}\bar{1}1)$ planes. STM images revealed ridges running along the $[11\ 0]$ direction that were 2.5 nm high and separated by 8 – 10 nm. These results indicate faceting into (111) and $(\bar{1}\bar{1}1)$ planes.

The structural characterizations of the $\text{CeO}_2(100)$ surface have not been definitive. Square, (1x1) LEED patterns have been published from $\text{CeO}_2(100)$ grown on $\text{Pd}(100)$ [106] and on $\text{SrTiO}_3(100)$. [14] Conceivably the surface terminations shown in Figure 7a and 7b would produce different LEED patterns, i.e. $p(1\times 1)$ vs. $c(2\times 2)$. However these authors made no claim as to surface termination. Overbury et al performed angle resolved low energy alkali ion scattering experiments.[19] They concluded that the $\text{CeO}_2(100)$ surface had a bulk termination with roughly 50% Ce ions on the surface and 50% O ions on the surface. Kim et al used direct recoil spectroscopy (DRS) / low energy ion scattering of Kr and concluded that the $\text{CeO}_2(100)$ surface was predominantly terminated by O.[14] Herman then used mass spectroscopy of recoiled ions (MSRI) and concluded that the structure depicted in Figure 7b was the most consistent with his results.[18] Yang et al imaged $\text{CeO}_2(100)$ grown on oxidized $\text{Cu}(111)$ by STM.[107] They observed step heights and atom spacing consistent with either Figure 7a or 7b. However they were using a positive sample bias which imaged the Ce cations. Therefore they couldn't say anything about the termination or O structure.

Nörenberg and Harding produced STM images of single crystal $\text{CeO}_2(100)$ at elevated temperatures.[21] They observed lines running in the $[011]$ direction. Atomic resolution along the lines had a spacing of 0.38 nm and the spacing between lines was 1.1 nm. These are equivalent to the spacing between O ions in the $[011]$ direction in Figure 7b and three times this spacing in the orthogonal direction. They called this fully oxidized surface a $\sqrt{2}/2(3\times 1)R45^\circ$ reconstruction. Based on the calculations they concluded that the surface was terminated by O. Their proposed structure was essentially equivalent to that shown in Figure 7b. The superstructure observed in the STM was due to small differences in the O height, i.e. a ripple, on the surface.

A high resolution electron microscopy study was conducted on CeO_2 nanocubes that had an edge length of ca. 20 nm.[108] Lin et al observed a variety of terminations on the (100) surfaces of these cubes. The $\text{CeO}_2(100)$ surface had regions of Ce, O and CeO termination. They also noted a pronounced tendency for atoms to hop along these surfaces.

A precise model for the $\text{CeO}_2(100)$ surface may not exist due to small energetic differences between different structures allowing a variety of terminations that may be in constant flux. However, an important result is that the surface is not terminated by a solid layer

of Ce or O as depicted in Figure 7a. Therefore a variety of O and Ce ions are exposed that have two, or more, coordination vacancies.

Both theoretical[8,9,13,93,97,100,109,110] and experimental[24,25,27,110-112] studies of the structure of reduced ceria surfaces have primarily focused on very low degrees of reduction, frequently single oxygen vacancies. O vacancies produce a reconstruction / relaxation around the vacancy with the remaining O ions that surround the vacancy displaced from their bulk termination positions. Multiple vacancies have been shown to organize into triangles and lines on $\text{CeO}_2(111)$. Nörenberg and Harding have reported a series of reconstructed STM and LEED images on $\text{CeO}_{2-x}(100)$ with up to 75% of the surface O removed from Figure 7a (50% removed from Figure 7b).[21] They proposed a series of structures resulting from an ordering of vacancies and a repositioning of the remaining O atoms on the surface. No long range order, either by LEED or STM, has been reported on other reduced, low-index surfaces.

4 – Cerium Oxide Thin Films

While there have been some studies of the adsorption and reaction of molecules on single crystal cerium oxide surfaces[75,83,113,114] the majority of studies have been conducted on cerium oxide thin films grown on a variety of substrates. In Section 4.1 the various methods that have been used to grow cerium oxide thin films will be described followed examples of specific crystallographic faces in subsequent sections. These sections will focus on studies where ceria films were grown and characterized. Adsorption studies on these surfaces will be covered in later sections.

4.1 – Methods

The production of a cerium oxide thin film requires the deposition of a Ce-containing precursor onto a dissimilar substrate. Organometallic precursors have been used in a process known as metalorganic chemical vapor deposition (MOCVD).[115,116] The solid molecular precursor is heated until a vapor is formed which is then transported by a carrier gas to the substrate. The transport lines are heated as well to prevent condensation. The precursor molecules are deposited on a heated substrate where they decompose in the presence of O_2 to create a ceria film. A variation of this method is to irradiate the substrate with a continuous wave infrared laser during deposition in a process termed laser chemical vapor deposition (LCVD).[117-119] The laser irradiation was found to enhance the growth rate of the films compared to the non-laser assisted MOCVD.

Inorganic precursors can also be used to deposit Ce on a substrate in a process known as spray pyrolysis. Cerium acetylacetonate[120] or cerium nitrate[121,122] were dissolved in water or an ethanol/water solution. The solution was then nebulized and sprayed onto the substrate. The deposited precursor was then thermally decomposed in air to produce the cerium oxide film.

Cerium oxide can be directly deposited from a CeO_2 target. CeO_2 is highly refractory so extraordinary means are needed to vaporize the target. E-beam heating[123-125], pulsed laser deposition (PLD)[15,19] and r.f. magnetron sputtering[126] have been used to ablate the ceria targets. Typically this has been conducted in an O_2 atmosphere to ensure complete oxidation of the deposited film.

The most common method of creating cerium oxide thin films is to start with cerium metal. Cerium is readily oxidized upon exposure to air and cannot be readily formed into wires as with many transition metals. Cerium can be evaporated by resistive heating in a Ta or W boat[20,37,127] or by e-beam heating[14,33,106,128]. Typically Ce is deposited in an oxidizing atmosphere such O_2 , [20] atomic O[33] or an O plasma[14] to produce CeO_2 on the substrate through reactive deposition. However there have been some cases where Ce was deposited directly on the surface followed by O_2 treatment to oxidize the Ce.[31,102,129]

In all of these methods the growth conditions have proven to be critical in determining the quality of the deposited film as will be discussed below.

4.2 – $\text{CeO}_2(111)$

The majority of work on cerium oxide thin films have utilized the $\text{CeO}_2(111)$ surface. One approach for creating a highly ordered ceria thin film is epitaxial growth of ceria on a single crystal substrate where the desired CeO_2 surface orientation has a good lattice match with the substrate. The cubic fluorite structure of CeO_2 has an excellent lattice match to the cubic diamond structure of Si, $\Delta a/a = 0.35\%$. Epitaxial films of $\text{CeO}_2(111)$ have been grown on Si(111) by PLD[130] and e-beam evaporation[123] of CeO_2 targets. The deposition was not performed in an O_2 ambient in order to avoid oxidation of the Si substrate.

$\text{CeO}_2(111)$ has been grown on cubic yttria-stabilized $\text{ZrO}_2(111)$ (YSZ(111)).[131-133] There is a 5.3% lattice mismatch between ceria and zirconia. However, it has been suggested that structural modifications such as dislocations, vacancies, interstitials and substitutions at the interface can reduce this misfit to ca. 1%.[134] Dmowski, et al suggested that strain due to the lattice mismatch is relieved by the formation of islands on the substrate separated by grain boundaries.[131] Maicaneanu, et al and Dmowski, et al cautioned that the catalytic properties of

these films are likely influenced by the structural defects and/or less stable surfaces between grains. Therefore the use of films grown on YSZ may not reflect the chemistry that occurs on other thin films surfaces or bulk single crystal terminations.

Most $\text{CeO}_2(111)$ films have been produced by evaporating Ce metal in an O_2 background onto the close-packed planes of hcp(0001) or fcc(111) single crystal metal surfaces. $\text{CeO}_2(111)$ has been grown on Pd(111)[129], Pt(111)[33,124,135], Rh(111)[35,36], Ru(0001)[16,20,37], Cu(111)[32,53,102,107,136,137], Ni(111) [20], and Au(111)[31]. Figure 9 shows STM images from a 3 nm thick $\text{CeO}_2(111)$ film grown on Ru(0001).[34] A relatively large area image, Figure 9a, shows that the $\text{CeO}_2(111)$ forms stacks of terraces up to several hundred nm in diameter. This morphology is similar to what was observed on single crystal $\text{CeO}_2(111)$ (Figure 8a). [104] The inset shows the hexagonal $p(1.4 \times 1.4)$ LEED pattern of $\text{CeO}_2(111)$ relative to the $p(1 \times 1)$ LEED pattern of Ru(0001). Figure 9b shows the atomic resolution of the $\text{CeO}_2(111)$ surface demonstrating the hexagonal ordering of the surface as well as isolated vacancies and defects.

It is perhaps surprising that the ceria not only forms well-ordered $\text{CeO}_2(111)$ but that the films are azimuthally aligned with the single crystal substrates as demonstrated by LEED and angle resolved low energy ion scattering. [20] The lattice mismatch between the $\text{CeO}_2(111)$ film and the metallic single crystal substrates ranges from 40% - 50%. Figure 10 shows STM images of a sub-monolayer film of $\text{CeO}_2(111)$ deposited on Rh(111).[35] The inset in Figure 10a shows a LEED pattern containing both the $p(1 \times 1)$ Rh(111) spots and the $p(1.4 \times 1.4)$ $\text{CeO}_2(111)$ spots. The spots observed in the STM image in Figure 10c are from the Ce cations. The spacing and symmetry are consistent with a $\text{CeO}_2(111)$ surface. A unique feature at this sub-monolayer coverage is the larger area superstructure evident in the lines produced in Figures 10b and 10c. These lines form a coincidence with the Rh(111) sublattice such that $5 \times a_{(\text{CeO}_2(111))} = 7 \times a_{(\text{Rh}(111))}$. There is evidently a strong interaction between the CeO_2 and the Rh that pins the oxide film at these coincidence points. A similar pattern for sub-monolayer ceria films has been observed on Cu(111)[32] and Ru(0001) (unpublished results).

Some care must be exercised in the formation and treatment of these films on some surfaces due to the interaction between the ceria and the substrate. Alexandrou and Nix reported that $\text{CeO}_2(111)$ films on Pd(111) decomposed at 600 °C via diffusion of Ce and O into the substrate.[129] Ceria films on Ni(111) lost a small amount of O following annealing at 700K and lost 25% of their O at 1000K.[20] The loss of O from the ceria is thought to be due to the formation of NiO. Annealing $\text{CeO}_2(111)$ films on Pt(111) in vacuum above 1000 K also results in reduction of the ceria.[33,41,124] It was also more difficult to produce fully oxidized ceria films at

sub-monolayer coverages of ceria. On Pt(111) it was suggested that the reduction / decomposition was due to the formation of Pt-Ce alloys.[41] A similar behavior was observed on Rh(111).[36] CeO₂(111) films grown on Cu(111) by deposition of Ce in O₂ at 520 K were stable up to 970 K in UHV but reduced at 1070 K.[137]

Various recipes have been proposed to improve the quality of the films, i.e. produce larger terraces with fewer defects. In general it appears that flatter films with wider terraces and fewer defects are produced by depositing Ce metal in an oxidizing environment while the substrate is maintained at elevated temperature. However, Staudt et al have reported that a continuous CeO₂(111) layer, as opposed to the stacks of plates depicted in Figure 9a, can be produced through a kinetically limited growth process of Ce in O₂ at 100 K followed by annealing in O₂ to 770 K.[136] Thicker films can be created by sequential homoepitaxial deposition and annealing steps.

4.3 – CeO₂(100)

CeO₂ has a good lattice match with SrTiO₃ however epitaxy is achieved by rotating the CeO₂ surface azimuthally relative to the SrTiO₃ substrate. CeO₂(100) has a 2% lattice mismatch with SrTiO₃(100) if the surfaces are rotated 45° with respect to each other so that [011] || [001]. CeO₂(100) has been grown on SrTiO₃(100) by e-beam evaporation of Ce metal in an oxygen plasma[14] and by PLD of a CeO₂ target.[19]

CeO₂(100) has been deposited on R-cut α-Al₂O₃ which exposes the (11 02) surface. The ceria was deposited by magnetron sputtering[126] or e-beam deposition[106] of CeO₂ and laser assisted chemical vapor deposition (LCVD).[119] CeO₂(100) was also grown on polycrystalline Al₂O₃[118] and amorphous SiO₂[117] by LCVD. However, although these films grew preferentially along the (100) direction they had a granular, columnar morphology with pyramidal caps that exposed (111) microfacets.

As noted above, CeO₂ has an excellent lattice match with Si. However, ceria thin films on Si(100) generally produced CeO₂(110) surfaces.[138-142] Growth of CeO₂(100) could be induced by biasing the Si(100) substrate during deposition by magnetron sputtering[143] or by irradiating the Si(100) substrate with an electron beam during deposition.[144]

There have only been a few reported examples of growing CeO₂(100) on the four-fold symmetric faces of fcc (100) metals. Tian et al deposited ceria films on Pd(100) by e-beam evaporation.[106] They produced CeO₂(100) if they used a CeO₂ source. However, multi-twinned CeO₂(111) films were produced if they deposited Ce metal in an O₂ atmosphere. We obtained similar results evaporating Ce metal from a resistively heated source in an O₂

background on Pd(100) and Pt(100) (unpublished results). Interestingly, the CeO₂(111) films produced following evaporation from a metallic Ce source demonstrated azimuthal registry with the (100) substrates producing 12 or 24 spot LEED patterns indicating CeO₂(111) domains rotated 0°, 45°, 90° and 135° with respect to the Pd(100) substrate.

CeO₂(100) was deposited by oxidative e-beam deposition of Ce metal on Ni foil that had been rolled to produce biaxially textured Ni(100) surface.[128] CeO₂(100) was also deposited by MOCVD on polycrystalline Hastelloy C276, a Ni-based multi-element alloy.[116] These studies were conducted with the goal of producing a CeO₂ buffer layer between metallic tape or wire-like substrates and high T_c metal oxide super conductors.

The results obtained with SrTiO₃(100), Pd(100), Pt(100) and biaxially textured Ni(100) suggest that the adsorption strength between the O in the film and substrate is a critical factor in determining whether film's structure is determined by the structure of the substrate or whether it forms the lower surface energy CeO₂(111) structure.

As noted above, CeO₂(100) has also been deposited on YSZ(100) with the same caveats mentioned previously regarding unique surface chemical properties related to defects and grain boundaries. [131]

4.4 – CeO₂(110)

In principle CeO₂(110) can be grown on SrTiO₃(110) if the two surfaces are rotated by 90° relative to each other so that [100] || [01 1]. As with CeO₂(100)/SrTiO₃(100) the two lattices would have a 2% lattice mismatch. Growth of this film has not yet been reported. CeO₂(110) was grown on SrTiO₃(211).[43] This is a stepped surface with two-dimensional symmetry where the spacing between the O ions in the short direction has a good lattice match to CeO₂(110). CeO₂(110) was also grown on Si(100)[138,140-142] and on YSZ(110). [131]

While there have been a number of reports of computational studies of adsorption and reaction on the CeO₂(110) surface there have not yet been any experimental studies reported.

5 – Adsorption on clean surfaces

5.1 - Inorganic molecules

5.1.1 – H₂ and H

H₂ can reduce CeO₂ powders at elevated temperatures at atmospheric pressure.[145,146] However, the consistent experimental observation on flat CeO_x surfaces under UHV conditions is that H₂ does not adsorb nor react.[19,147,148] This is despite

theoretical calculations that indicate that H_2 will adsorb and dissociate exothermically on $CeO_2(111)$ and $CeO_2(110)$. [99,149]

Exposure of stoichiometric $CeO_2(111)$ to atomic D at 115 K produces $-OD$ on the surface at low exposure. [148] This process leads to the reduction of Ce^{4+} to Ce^{3+} . At higher exposure (> 50 L) water is observed in O 1s XPS indicating that $D(g)$ impinging on the surface reacted with OD to produce chemisorbed D_2O . The OD disproportionated to produce $D_2O(g)$ between 200 K and 600 K. The chemisorbed water desorbed in a relatively sharp peak near 200 K. D_2 desorbed in a broad, weak feature between 400 K and 500 K. On reduced $CeO_{2-x}(111)$ exposure to $D(g)$ again produced OD on the surface but the tendency to form $D_2O(a)$ at higher exposures decreased as the surface became more reduced. The OD adsorbed on the reduced $CeO_{2-x}(111)$ surface was stabilized compared to that on a fully oxidized $CeO_2(111)$ surface. Water and D_2 both desorbed near 570 K. These observations are supported by DFT calculations which determined exothermic adsorption of $H(g)$ on the surface O anions on $CeO_2(111)$ and $CeO_2(110)$ accompanied by the reduction of the neighboring Ce cations. [150] Ultra accelerated quantum chemical molecular dynamics simulations indicated that $H(g)$ will initially form OH on the $CeO_2(111)$ and (110) surfaces followed by reaction with additional $H(g)$ to produce $H_2O(a)$. [151]

5.1.2 – O_2

One of the principle applications of CeO_2 is as an oxygen storage material in automotive exhaust catalysts. [4] In this capacity the ceria acts as a buffer to supply O during fuel-rich / O_2 deficient periods of engine operation, and conversely remove O when there is an excess of O_2 in the exhaust stream. It is believed that oxidation reactions over ceria surfaces occur through a Mars van Krevelen mechanism wherein an adsorbate reacts with O contained in the substrate and this O is subsequently replenished by O_2 from the gas phase. [152,153] As such it is important to understand both the adsorption and dissociation of O_2 with ceria surfaces and the desorption of O_2 from oxidized ceria.

It has been shown that the oxidation of Ce metal proceeds at below 300 K through the formation of Ce_2O_3 which is then capped by a thin layer of CeO_2 on the surface. [154-156] Heating a polycrystalline sample that was capped with a layer of CeO_2 to 600 K resulted in a reduction of the surface to Ce_2O_3 based on Ce 3d and Ce 4d XPS. [43] Conversely, a $CeO_2(100)$ surface that was reduced by Ar^+ ion sputtering at 300 K showed partial re-oxidation when it was heated to 600 K in vacuum. [19] These two results are indicative of O re-distribution between the surface and the bulk below 600 K.

Wu et al studied the adsorption of O₂ on ceria nanoshapes.[157] Nanorods, nanocubes and nano-octadra are believed to expose primarily {110}+{100}, {100} and {111} faces, respectively.[157] Using Raman spectroscopy they observed superoxo (O₂⁻) and peroxo (O₂²⁻) species on the reduced CeO_{2-x} surfaces. The same species were also observed on reduced, non-shape-specific CeO_{2-x} powders.[158] These species dissociated into lattice O²⁻ and re-oxidized the surface. The reaction pathway was:

In addition to the dissociation, approximately 20% of the adsorbed oxygen desorbed as O₂. This occurred through disproportionation reactions.

The O₂ desorption occurs at a lower temperature on the nanocubes, ca. 340 K, than on the nanorods, ca. 470 K. The temperature dependent Raman spectroscopy further indicated that the superoxo species disappeared before the peroxo species.

DFT calculations on stoichiometric CeO₂(111) indicated that the adsorption of O₂ was endothermic.[158] DFT + U calculations on partially reduced CeO_{2-x}(111) indicated that the superoxo species was weakly bound to the O-vacancy (-0.30 to -0.38 eV) and the peroxo species is more strongly bound (-2.80 to -3.25 eV).[159] Similar calculations on partially reduced CeO_{2-x}(110) and CeO_{2-x}(100) surfaces reported only the peroxo species with adsorption energies of -2.05 eV and -2.02 eV, respectively.[160]

Putna et al observed desorption of O₂ between 800 K and 1200 K from ceria films deposited on α-Al₂O₃(0001) whereas no O₂ desorbed below 1300 K from single crystal CeO₂(111).[161] This suggests that the morphology and defect structure of the ceria surface further influences the adsorption and desorption of O₂.

5.1.3 – H₂O

Water is ubiquitous in many catalytic reactions either as a reactant, product, solvent or simply a spectator present in the atmosphere. It is also the simplest example of a molecule

possessing the hydroxyl moiety, R-OH, and its interactions with ceria surfaces provide important information for understanding the adsorption and reaction of more complicated molecules such as alcohols and carboxylic acids.

Experimental studies of water adsorption on stoichiometric CeO₂(111) and CeO₂(100) have concluded that the water adsorbs molecularly, dissociatively or a mixture of both.[15,51,68,133,148,162-164] Computational studies of water adsorption on CeO₂(111) have been contradictory. Watkins et al.[149] concluded water will dissociate while Fronzi et al.[165] and Marrocchelli and Yildiz[166] concluded it would not. Molinari et al. compared water adsorption on CeO₂(111), (100) and (110) using DFT-GGA+U calculations.[167] They concluded that dissociation was favored over molecular adsorption, and the dissociated state was the most stable on the CeO₂(100) surface. They also reported that molecular adsorption becomes more favorable as the water coverage increases. Fernández-Torre et al compared calculations using a number of different approximations for handling exchange and correlation within DFT and concluded that there was very little difference between the dissociated species and molecular water in the lowest energy configuration.[168]

The primary method for differentiating molecular water from dissociated -OH on the surface has been O 1s XPS data.[15,51,68,133,148,162-164] As shown in Figure 11a, water adsorption on CeO₂(111) and CeO₂(100) near 200 K results in three O 1s peaks. The lowest binding energy peak at 530.5 eV is from the lattice O in CeO₂. The highest binding energy peak near 534.4 eV is associated with molecular water. This water could either be chemisorbed water or multilayer / physisorbed water. Since the spectra were recorded above 180 K this feature is unlikely associated with multilayer water since multilayer water has generally been reported to desorb between 150 K and 170 K.[169] The intermediate feature near 532 eV has generally been assigned to -OH although it has also been assigned to chemisorbed water[68] or a combination of -OH and chemisorbed water.[162] Valence level photoelectron spectra have demonstrated that the feature near 532 eV is associated with -OH and not H₂O.[15] The O 1s spectra from water on CeO₂(111) (black curve) indicates a nearly equal amount of molecular water and -OH which is consistent with calculations that indicate little energetic difference between molecular and dissociative adsorption. The O 1s spectra from water on CeO₂(100) (blue curve) indicates that the water predominantly dissociated on this surface which is consistent with Molinari et al's calculations.[167]

The TPD following water adsorption at 180 K on oxidized CeO₂(111) and CeO₂(100) are very different as shown in Figure 11b. On CeO₂(111) the water mostly desorbs in a single, sharp feature near 200 K.[15,68,133,148] On CeO₂(100) the water desorption extends from near 200

K to beyond 500 K.[15] The principal conclusion from these results is that hydroxyls are more stable on oxidized $\text{CeO}_2(100)$ than on $\text{CeO}_2(111)$. This result is reasonable if we consider how the dissociated water would fill the coordination vacancies indicated in the surface structures shown in Figures 6 and 7b. On $\text{CeO}_2(111)$ the Ce and the O each have a single coordination vacancy whereas on $\text{CeO}_2(100)$ these surface ions each have two coordination vacancies. OH + H are most stable when they bond to the more under-coordinated surface species. This intuitive conclusion is supported by the calculations of Molinari et al.[167] They reported that the dissociated state was most stable on $\text{CeO}_2(100)$.

Chen et al compared hydroxyls formed when water adsorbed on $\text{CeO}_2(111)$ with hydroxyls formed by exposure to atomic D. [148] In this case the hydroxyls adsorb in two different configurations. Following water dissociation the hydroxyls populate a mixture of three-fold sites originally occupied by the surface O and singly coordinated sites atop the second layer Ce. When the surface is exposed to atomic D, all of the –OD occupies the three-fold adsorption sites. When D_2O was adsorbed, rather than atomic D, the water desorbed in a manner similar to that shown by the black curve in Figure 11b. When the surface was exposed to atomic D, the water initially desorbed at low exposure of D in a broad feature from 200 K to 600 K. At high D exposure a more pronounced peak appeared near 200 K. In combination with their O 1s data they concluded that the broad desorption was due to disproportionation of hydroxyls on the surface producing D_2O and an O-vacancy. The peak near 200 K was produced by reaction between –OD and impinging D that produced chemisorbed water at low temperature.

There have been two experimental studies of water adsorption on oxidized $\text{CeO}_2(100)$. Herman et al. concluded that water adsorbed both molecularly and dissociatively and that all of the water desorbed below 350 K.[163] As shown by the blue lines in Figure 11b, Mullins and Albrecht reported water desorption extending to nearly 600 K.[15]

Ceria is known for its ability to liberate O through the reduction of Ce^{4+} to Ce^{3+} . When this occurs on $\text{CeO}_{2-x}(111)$, the O-vacancies create Ce cations with two coordination vacancies and a three-fold hollow adsorption site.[103] Experiment[15,51,68,148,162,164] and theory[149,165-167] have generally concluded that the presence of vacancies on $\text{CeO}_{2-x}(111)$ promotes and stabilizes the dissociation of water. As shown in Figure 12a there is considerably more –OH on $\text{CeO}_{1.7}(111)$ than on $\text{CeO}_2(111)$ (Figure 11a). The hydroxyls are stable to above 500 K compared to oxidized $\text{CeO}_2(111)$ where they mostly disappear by 250 K. [15,51,68,148] As seen in Figure 12b, reaction between hydroxyls on $\text{CeO}_{1.7}(111)$ results primarily in H_2 desorption. [15,68,148] Henderson et al. observed no H_2 desorption from reduced $\text{CeO}_{2-x}(111)$ and Ce 3d XPS indicated further reduction of the Ce in response to water adsorption.[133] One

possible explanation for the differences reported by Henderson et al and these other studies is the nature of the $\text{CeO}_{2-x}(111)$ films. Henderson et al grew their films on yttrium-stabilized $\text{ZrO}_2(111)$ (YSZ). The other films were grown on $\text{Ru}(0001)$ [15,68] or $\text{Cu}(111)$.[51,148] Ferrizz et. al. have reported that ceria films grown on YSZ(100) showed greater reducibility than films grown on $\alpha\text{-Al}_2\text{O}_3(0001)$.[170] The source of the enhanced reducibility on YSZ was unclear; but if a similar effect is occurring on YSZ(111), this enhanced reducibility presumably indicates a lower O-vacancy formation energy, thereby producing a smaller driving force to re-oxidize a reduced surface through water decomposition. Enhanced reducibility of $\text{CeO}_2(111)$ grown on YSZ may also explain why Henderson et al. were able to reduce their films by annealing to 830 K, whereas other authors have reported thermal reduction only at much higher temperatures.[23,111]

The desorption of primarily H_2 from water adsorbed on reduced $\text{CeO}_{1.7}(111)$ is in contrast to the desorption from reduced $\text{CeO}_{1.7}(100)$ where the primary desorption channel is still recombination to produce water with only a small amount of H_2 formation (Figure 12b). The vacancy formation energy is higher on $\text{CeO}_2(111)$ than on $\text{CeO}_2(100)$.[7,8] Therefore it would be anticipated that the driving force for filling the vacancy would be greatest on $\text{CeO}_{2-x}(111)$.

5.1.4 – CO and CO_2

CO can reduce ceria powder and nanocrystals at elevated temperatures producing CO_2 and CeO_{2-x} . The oxidation of CO is also one of the reactions promoted by ceria in automotive exhaust catalysts and in the water-gas shift reaction.[4] However, as with H_2 , CO does not adsorb on either $\text{CeO}_2(111)$ or $\text{CeO}_2(100)$ in UHV.[171-173] Weak adsorption of CO on the different faces of CeO_2 is consistent with numerous calculations which have found that the adsorption energy is ca. 0.2 eV.[174-180] Several authors have calculated exothermic reaction energies greater than 2 eV for the formation of carbonate from CO on $\text{CeO}_2(110)$ [175,178-180] Nolan and Watson further determined that carbonate formation would be more exothermic on $\text{CeO}_2(100)$, -3.2 eV, than on $\text{CeO}_2(110)$, -1.95 eV.[180] To date there have been no measurements of CO adsorption on $\text{CeO}_2(110)$. Stubenrauch and Vohs have reported that CO does not adsorb on single crystal $\text{CeO}_2(100)$ at 300 K[171] and we have obtained unpublished results that indicate that ca. 0.1 ML of CO adsorbs on a $\text{CeO}_2(100)$ thin film at 100 K that then fully desorbs by 200 K.

CO_2 adsorption and activation offers a number of intriguing applications. CO_2 adsorption could provide a means to capture and sequester this greenhouse gas from the atmosphere.

Activation of CO_2 to release O could conceivably be used as an oxidant in organic oxidation reactions and produce CO as a syngas reactant for further synthesis reactions.

Senanayake and Mullins observed that CO_2 interacts weakly with stoichiometric $\text{CeO}_2(111)$.^[71] At 90 K CO_2 primarily physisorbed and then desorbed by 150 K. A small amount of carbonate was formed that persisted up to 300 K. Senanayake et al studied CO_2 on reduced CeO_{2-x} clusters on $\text{Au}(111)$ and observed similar behavior with a small amount of carbonate formed at low temperature that persisted up to 300 K. Neither paper reported whether the CO_2 simply desorbed as CO_2 or whether on the reduced surface it was reduced to CO leaving the O with the ceria. In two papers Lykhach et al^[181] and Staudt et al^[182] examined the re-oxidation of reduced $\text{CeO}_{2-x}(111)$ grown on $\text{Cu}(111)$. Only a small amount of carbonate and carboxylate were observed in the C 1s and O 1s spectra^[181] however a significant amount of Ce^{3+} was oxidized to Ce^{4+} .

A more recent study of CO_2 on $\text{CeO}_x(100)$ has revealed a much stronger interaction of CO_2 with both the oxidized and reduced surfaces.^[72] Figure 13 shows the CO_2 TPD from stoichiometric $\text{CeO}_2(100)$ (black line) and reduced $\text{CeO}_{1.7}(100)$ (blue line) following CO_2 exposure at 180 K. On the oxidized surface the CO_2 desorbs in a series of peaks at 230 K, 410 K, 510 K and 655 K. The rising tail above 750 K resulted from desorption from the sample holder. C 1s XPS and C k-edge NEXAFS spectra indicate that the CO_2 is adsorbed as carbonate throughout the entire range. The 230 K peak conceivably corresponds to the weak CO_2 adsorption observed on $\text{CeO}_2(111)$.^[71] A unique feature that was revealed in the C k-edge NEXAFS spectra is that the molecular plane of the carbonate is oriented parallel to the $\text{CeO}_2(100)$ surface (Figure 14). DFT+U calculations were conducted on possible adsorption states for the carbonate and the most stable configuration was a tri-dentate species where the C in the CO_2 bonded to a surface O and the O in the CO_2 bonded in bridge sites to surface Ce. This species is shown in the inset in Figure 14. The adsorption energy for this carbonate was -1.93 eV. When the $\text{CeO}_2(100)$ surface is reduced to $\text{CeO}_{1.7}(100)$ the low temperature CO_2 desorption is largely suppressed and the carbonate is stabilized producing a prominent peak at 765 K (Figure 13, blue line). No CO desorbed from either the oxidized or reduced surface and the Ce 4f peak intensity didn't change on the reduced surface indicating that CO_2 did not re-oxidize the $\text{CeO}_{1.7}(100)$ surface.

Hahn et al investigated the adsorption of CO_2 on a stoichiometric $\text{CeO}_2(111)$ surface using DFT and DFT+U calculations.^[183] They found that a monodentate carbonate species was the most stable configuration but was weakly adsorbed with an average binding energy of ca. -0.3 eV for both methods. They didn't examine adsorption on a reduced surface. Cheng et al

have studied CO₂ adsorption on oxidized and reduced CeO_x(110) using the DFT+U formalism.[184] Eleven different configurations were examined for CO₂ adsorbed on the stoichiometric CeO₂(110) surface. The most stable configuration had the CO₂ molecule bridging between Ce⁴⁺ cations with an adsorption energy of -0.26 eV. The C=O bond distance and the distance between the CO₂ molecule and the surface indicated that the molecule was physisorbed as CO₂ and did not form a carbonate. They considered two different models for the reduced CeO_{2-x}(110) surface. In one an in-plane O-vacancy was formed by simply removing an O from the surface. In the other a split vacancy was produced when an O adjacent to the initial vacancy shifts toward that vacancy into a bridge site between two Ce cations. CO₂ bonds to the surface with the in-plane vacancy as a carboxylate with the C and one O atom in the molecule bonding to two Ce cations (Figure 15a). The adsorption energy is -1.04 eV. CO₂ adsorption on a surface with the split vacancy forms a monodentate carbonate (Figure 15b) and has a more stable adsorption energy of -1.22 eV.

5.1.5 - NO_x

The adsorption and reaction of nitrogen oxides (NO_x), i.e. N₂O, NO and NO₂, were among the first adsorbate systems investigated on ceria surfaces. This was because of ceria's application in automotive exhaust catalysts and the further potential for ceria in NO_x remediation.

Ferriz et al reported that NO did not adsorb at 300 K on a stoichiometric CeO₂(111) single crystal or on CeO₂ grown on α-Al₂O₃(0001).[185] Overbury et al also observed that NO did not adsorb on CeO₂(100) at 160 K or 300 K[19] but adsorbed weakly at 90 K on oxidized CeO₂(111) / Ru(0001).[59] As shown at the bottom of Figure 16 most of the NO desorbs as NO below 200 K with small amounts of N₂ and N₂O desorbing in the same temperature range. The broad NO desorption between 300 K and 400 K was ascribed primarily to NO adsorbed on the sample holder and on the back of the Ru(0001) crystal. This weak adsorption on the oxidized surface is consistent with the calculations of Yang et al who reported that NO adsorbs atop the Ce⁴⁺ cation on CeO₂(111) with an adsorption energy of only -0.1 eV. N 1s XPS indicates that at 90 K the NO adsorbs on CeO₂(111) as N₂O and [NO₂]⁻ as shown in Figure 17a. These may be slightly more stable surface products that were not explored in the calculations of Yang et al.

Both Ferriz et al[185] and Overbury et al[19,59] reported that NO adsorbs more strongly on reduced CeO_{2-x}. These observations on low-index, low-surface area CeO_{2-x} surfaces confirm the work by Daturi et al which correlated catalytic deNO_x activity on ceria powders with O-vacancy concentration on the ceria surface.[186] Ferriz et al observed only N₂ desorption

following NO adsorption at 300 K on reduced $\text{CeO}_2 / \alpha\text{-Al}_2\text{O}_3(0001)$. The N_2 desorption profile varied depending on how they prepared their reduced surface. A film that was grown in a lower O_2 ambient pressure resulted in a sharp N_2 desorption between 300 K and 400 K. A fully oxidized film that was sputtered to preferentially remove O produced a broad N_2 desorption that extended from 400 K to 800 K. Overbury et al observed a variety of desorption products and the product distribution varied depending on adsorption temperature.[59] As shown in the top of Figure 16, following adsorption at 90 K NO, N_2 and N_2O are produced primarily below 200 K with additional NO and N_2 desorbing between 200 K and 400 K. When the adsorption temperature is raised to 150 K the low temperature desorption is suppressed and additional N_2 desorption is observed near 350 K. When the adsorption temperature is increased to 400 K, which is above where most products were observed following adsorption at lower temperatures, new desorption features appear with a substantial amount of N_2 as well as NO desorbing in a pair of peaks at 500 K and 740 K.

The N 1s XPS spectra reveal how the surface species differ following adsorption at different temperatures on reduced $\text{CeO}_{2-x}(111)$ (Figure 17b). Following adsorption at 90 K two stable surface species are observed; N_2O with its two inequivalent nitrogens producing a doublet at 404.6 eV and 408.3 eV, and NO^- at 402.6 eV. These species mostly desorb and produce the products observed below 200 K. When the adsorption temperature was raised to 145 K the N_2O surface species is suppressed and the NO adsorbs almost exclusively as NO^- . As the adsorption temperature is raised further new surface species appear and at 350 K nitride, N^{3-} , is nearly the only species evident. These results suggest that the decomposition of NO^- leads to N_2 and NO desorption between 200 K and 400 K. Decomposition of N^{3-} produces the products at 500 K and 740 K. Ferriz et al conjectured that the $\text{CeO}_{2-x} / \alpha\text{-Al}_2\text{O}_3(0001)$ grown in a lower oxygen pressure was less reduced than the sputtered $\text{CeO}_{2-x} / \alpha\text{-Al}_2\text{O}_3(0001)$ film. [185] The less highly reduced film produced primarily NO^- that decomposed to N_2 below 400 K whereas the more highly reduced film resulted in nitride formation that decomposed between 400 K and 800 K.

Yang et al calculated that the adsorption energy of NO on a reduced $\text{CeO}_{2-x}(111)$ surface will be an order of magnitude greater than on the oxidized surface.[187] The most stable configuration is with the O end down filling the O-vacancy on the reduced surface. They report that the decomposition of $2\text{NO(a)} - \text{CeO}_{2-x}$ to N_2 plus re-oxidized CeO_2 is thermodynamically favorable. Overbury et al noted that NO in fact re-oxidizes $\text{CeO}_{2-x}(111)$ at 300 K based on Ce 4d XPS.[59] However, the ceria became less oxidized upon annealing to 500 K. This was ascribed to O transport from the surface into the bulk. Interestingly, Berner et al did not observe re-

oxidation of reduced CeO_{2-x} / Pt(111) following exposure to NO at either 300 K or 400 K.[67] They attribute the lack of re-oxidation compared to the results of Overbury et al to a different morphology of the ceria. They propose that in their system the ceria forms islands with the reduced Ce^{3+} sites situated and conceivably stabilized at the Pt/ceria interface.

NO_2 is an aggressive oxidant and is generally more effective than even O_2 . Berners et al observed that NO_2 oxidized reduced CeO_{2-x} / Pt(111) whereas NO did not.[67] Rodriguez et al reported NO_2 forms nitrate, $[\text{NO}_3]^-$, at 300 K on polycrystalline CeO_2 films deposited on Pt(111).[188] Namai et al did not observe any adsorbates following NO_2 exposure on single crystal $\text{CeO}_2(111)$ at room temperature using non-contact atomic force microscopy.[113] On lightly reduced $\text{CeO}_{2-x}(111)$ they observed that the O-vacancies were healed following NO_2 exposure which they attributed to the reaction of NO_2 with the vacancy to produce NO gas. They also observed adsorbed features that they assigned to $[\text{NO}_3]^-$. When reduced CeO_{2-x} / Pt(111) was exposed to NO_2 Rodriguez et al observed adsorbed NO and N (possibly nitride) as well as nitrate.[188] Nolan et al have calculated the structures of the adsorbed species for NO_2 on reduced $\text{CeO}_{2-x}(111)$, (110) and (100).[189] They determined that NO_2 adsorbs as $[\text{NO}_2]^-$ on all three surfaces. They do not report the formation of $[\text{NO}_3]^-$ nor the cleavage of an N-O bond which they conclude must be an activated process that could occur between 300 K and 400 K.

N_2O was studied on a sputter reduced $\text{CeO}_{2-x}(100)$ film. The dominant surface species at 100 K was N_2O with a small amount of NO^- . [59] Evolution of N_2 was observed during exposure to N_2O at 90 K which is consistent with the formation of NO^- . The adsorbed N_2O desorbs by 150 K with a small amount of N_2 produced as well. Müller et al have calculated the adsorption of N_2O on stoichiometric $\text{CeO}_2(111)$ using a number of different formalisms.[190] The molecule always adsorbs linearly on a Ce^{4+} cation but the calculations differ as to whether it adsorbs with an O or a N bound to the cerium depending on the method used. In any case the adsorption is weak with an adsorption interaction of only -0.2 eV to -0.3 eV. They cite experimental vibrational data that indicate that the preferred orientation is with the O toward the cerium.

5.1.6 – SO_2 and H_2S

The finite concentration of sulfur containing molecules in fossil fuels leads to the formation of sulfur oxides (SO_x) in the exhaust. Adsorption of these gases leads to loss of oxygen storage capacity in the cerium oxide in automotive catalytic converters. However, high affinity for SO_x could be exploited by trapping sulfur in the effluent.

Two studies examined the adsorption of SO₂ on cerium oxide thin films and arrived at different conclusions. Overbury et al used well-characterized CeO₂(111) / Ru(0001) and concluded that SO₂ adsorbed as SO₃²⁻ on the fully oxidized surface at temperatures from 100 K – 600 K.[191] Based on S 2p XPS it was concluded that the SO₂ adsorbed through a Lewis acid – base interaction at the basic O²⁻ surface sites. The adsorbate desorbed as SO₂ over this entire range with major desorption peaks near 200 K and 400 K. There was no evidence of either oxidation to SO₄²⁻ or reduction to SO²⁻ or S²⁻. These results were consistent with an earlier study by Waqif et al on CeO₂ powders where they observed by vibrational spectroscopy that only sulfite formed following room temperature exposure to SO₂. [192] Sulfate formation occurred after exposure at 673 K and was promoted by simultaneous exposure to O₂. Contrary to these reports, Rodriguez et al found that SO₂ adsorbed almost exclusively as SO₄²⁻ on fully oxidized, polycrystalline CeO₂ / Pt(111). [193]

Perhaps in an effort to resolve this discrepancy a number of other investigators performed additional experiments that investigated additional parameters in the interaction between SO₂ and ceria. Smirnov et al studied SO₂ adsorption on polycrystalline CeO₂ deposited on Al₂O₃ using an SO₂ pressure of 2.5 mbar. [194] They observed sulfite formation at temperature below 473 K and sulfate formation above 573 K. When an equal pressure of O₂ was added to the SO₂ exposure sulfite formation was suppressed at the lower temperatures but sulfate still only appeared at the higher temperatures. The sulfate formation was enhanced by the addition of O₂ at the higher temperatures, however. Ferriz et al used polycrystalline ceria films deposited by spray pyrolysis on Ta foil, used for TPD measurements, and by Ce vapor deposition in an O₂ ambient onto a Mo(100), used for XPS measurements. Following SO₂ exposure at 298 K a prominent SO₂ desorption peak was observed near 473 K. [195] This is similar to the SO₂ desorption reported by Overbury et al. [191] However, distinct SO₂ desorption peaks were also observed between 800 K and 1000 K that were not seen by Overbury et al. When the SO₂ exposure temperature was increased to 573 K the higher temperature peak increased in intensity and the lower temperature peak was suppressed. The S 2p XPS indicated that the SO₂ adsorbed predominantly as sulfite at 298 K but some of this transformed to sulfate as the sample was heated. Heating to 923 K further transformed the sulfate into sulfide. Similar results were obtained regardless of whether the SO₂ was co-exposed with O₂ or by itself.

Most recently, Happel et al studied SO₂ on well-characterized CeO₂(111) / Cu(111). [196] Their S 2p XPS results, shown in Figure 18a, indicate that sulfite is the primary surface species at 300 K. As the sample was heated some of the sulfur was reduced to S⁰ and S²⁻. No sulfate was observed at any temperature.

The consensus is that sulfite is the primary species adsorbed at room temperature and below. Elevated temperature, co-exposed O_2 and perhaps surface heterogeneity appear to promote sulfate formation. This is consistent with the DFT-U calculations conducted by Lu et al.[197] SO_3^{2-} was determined to be the most stable species on $CeO_2(111)$ whereas SO_4^{2-} was also formed on $CeO_2(110)$. This difference was attributed to the spacing between O^{2-} anions on the two surfaces. Sulfites formed by attaching to a single O^{2-} anion in a monodentate configuration. On $CeO_2(110)$ sulfates formed by bridging between two O^{2-} anions. The spacing between the O^{2-} anions is too great on $CeO_2(111)$ for this two occur. A stable sulfate configuration can occur on $CeO_2(111)$ if the sulfite extracts an O from the surface to create SO_4^{2-} . This is an activated process which is consistent with the observation that sulfate formation generally requires elevated temperature. The cases where sulfate was observed at lower temperatures may be related to heterogeneous surfaces that were not exclusively $CeO_2(111)$.

Adsorption on a reduced CeO_{2-x} surface promotes reduction of the SO_2 . As shown in Figure 18b the SO_2 again adsorbs on $CeO_{2-x}(111)$ / $Cu(111)$ primarily as SO_3^{2-} at 300 K but S 2p features that can be assigned to SO_2^- , S^0 and S^{2-} are also apparent. As the sample is annealed most of these species convert to the sulfide. Overbury et al observed that there were virtually no products desorbed from a heavily reduced $CeO_{2-x}(111)$ surface following SO_2 exposure. In Figure 18b sulfide is identified at two slightly different binding energies; surface sulfide occurs at 160.7 eV and bulk sulfide is at 161.3 eV. The surface sulfide transforms into a bulk sulfide at elevated temperature. Overbury et al observed that upon annealing to 1000 K the S 2p signal mostly disappeared as the S diffused away from the near-surface region sampled by the sXPS.[191] Happel et al[196] and Overbury et al[191] both observed that Ce^{3+} oxidized to Ce^{4+} as sulfur was reduced from S^{4+} to S^{2-} . Using DFT+U calculations Kullgren et al concluded that SO_2 adsorption will lead to sulfide formation on reduced $CeO_{2-x}(111)$ but will still lead to sulfate formation on $CeO_{2-x}(110)$. [198]

H_2S provides additional insight into the interaction of S-containing species with ceria surfaces. It is also a close analog to water and the adsorption and dissociation of H_2O and H_2S on $CeO_2(111)$ have been compared computationally.[166,199] Unlike SO_2 , H_2S interacts with $CeO_2(111)$ as a Lewis base with the basic S atom bonding to the acidic Ce^{4+} cation. As shown in Figure 19a the S 2p XPS indicates the presence of H_2S on the ceria surface from 100 K – 150 K but none at 200 K.[200] In addition to H_2S the S 2p spectrum also indicates $-SH$. The intensities of both the H_2S and $-SH$ decrease as the sample is annealed from 100 K to 200 K. This is consistent with TPD spectra that show H_2S desorption at ca. 165 K from oxidized

CeO₂(111).[200] As can be seen in Figure 19b, O 1s spectra recorded at the same temperatures as the S 2p spectra indicate the formation of H₂O and –OH on the CeO₂(111) surface. These are formed from the dissociated H from the H₂S bonding with the surface O on the ceria. TPD spectra show water desorption occurring from 200 K to 400 K as these react and desorb from the surface. The presence of both –SH and –OH therefore leads to competitive reaction pathways producing H₂S and H₂O. As the reactions between –SH and –OH proceed as the surface is heated the S is transformed into surface sulfide. The binding energy is consistent with the surface sulfide observed during SO₂ decomposition in Figure 18a.

The calculations of Chen et al[199] and Marrocchelli and Yildiz[166] are consistent with the observed experiments with H₂S adsorbing weakly molecularly and progressing through more stable –SH and S adsorption species. Note that the S 2p spectra at 200 K and above do not give any indication of SO_x species on the surface. Chen et al found that –SH is most stable when bound atop a surface O whereas Marrocchelli and Yildiz determined that the most stable configuration for –SH was atop the Ce. Chen et al further reported that desorption of SO₂ is favorable whereas Marrocchelli and Yildiz determined that formation of H₂(g), H₂O(g) and SO₂(g) were all equally unfavorable. Marrocchelli and Yildiz suggested that the formation of SO₂ was disfavored due to the high vacancy formation energy in CeO₂(111). The formation of H₂O was slightly exothermic when the S filled the vacancy created by the H₂O formation but that there was a large activation barrier in this step.

When the ceria surface is partially reduced considerably more H₂S adsorbs on the surface and decomposition to –SH and S is observed at 100 K.[200] TPD spectra show that H₂O desorbs near 580 K when the ceria is 20% reduced (CeO_{1.9}(111)), reaches a maximum intensity when the ceria is 50% reduced (CeO_{1.75}(111)) and then decreases in intensity at higher degrees of reduction.[200] H₂ desorption occurs at 580 K when the degree of reduction is greater than 50% and increases at the expense of H₂O formation at higher degrees of reduction. Marrocchelli and Yildiz determined that while H₂(g) may be thermodynamically more favorable than H₂O(g), it has a significantly higher activation barrier and thus would not be anticipated.[166] They ascribe the transition from H₂O formation to H₂ to increasing difficulty to remove O from the surface as the ceria becomes more reduced.

The production of water at elevated temperature from H₂S on partially reduced CeO_{2-x}(111) is in contrast to the behavior of H₂O where H₂ desorption is almost exclusively observed at elevated temperature with little H₂O.[68,148] Mullins and McDonald attributed the difference between H₂S and H₂O to the ability of O to diffuse into the bulk compared to S.[200] At the temperature where –OH reacts, i.e. near 580 K, the O can diffuse into the bulk[68] whereas S

moves from the surface to the bulk at higher temperatures.[63,191,200] The stability of S on the surface makes the surface more oxidized and thus makes it easier to remove the O.

5.2 – Organic Molecules

Organic molecules appear to require a functional group containing a heteroatom such as N, O, S, etc. in order to adsorb and react on ceria surfaces under UHV conditions. Non-functionalized organic molecules have not been extensively studied. It was reported that ethylene desorbs molecularly below 150 K on CeO₂(111).[201] Ethylene was also studied on Rh / CeO₂ / YSZ(100).[202] While the authors didn't explicitly report the ethylene interaction with a clean ceria surface, the results were interpreted in terms of ethylene adsorption on the Rh particles. Vile' et al reported the selective hydrogenation of alkynes to olefins at high conversion over polycrystalline ceria powders.[203] Carrasco et al investigated this system computationally examining the hydrogenation of acetylene to ethylene over CeO₂(111) by DFT.[204] They determined that β -C₂H₂ radical species adsorb on-top of surface oxygen atoms leading to C₂H₃ species. This species has a lower activation barrier leading to gas phase C₂H₄ compared to the formation of a β -C₂H₄ radical that would lead to more highly hydrogenated products.

Of the functionalized molecules the oxygenates; alcohols, aldehydes, ketones, ethers and carboxylic acids, have been by far the most investigated. There have been several reviews covering adsorption and reaction of some of these molecules.[11,12,205] In Section 5.2.1 the adsorption and reaction of these molecules will be covered more extensively. In Section 5.2.2 organic adsorbates containing other functional groups will be reviewed.

5.2.1 - Oxygenates

5.2.1.1 Alcohols

Methanol has been the most extensively investigated organic oxygenate on ceria surfaces. This is because, as stated by Badlani and Wachs, "methanol is a 'smart' chemical probe molecule that can provide fundamental information about the number of surface active sites, the nature of surface active sites, the decomposition temperature of surface methoxy intermediates and the quantitative TOF values for methanol oxidation for pure metal oxide catalysts." [206] It therefore serves as an ideal probe for comparing ceria surfaces to the surfaces of other oxides and differentiating the adsorption and reaction characteristics between different ceria surfaces. The chemically important reaction for the adsorption of methanol on ceria is the formation of methoxy and hydroxyl:[11,12,83,102,207,208]

The methoxy species can be differentiated spectroscopically from the alcohol based on the C 1s, and especially the O 1s, binding energies.[50,208]

In contrast, calculations by Mei et al have indicated that the most stable dissociative state on stoichiometric CeO₂(111) involves cleavage of a C-H bond and the formation of a C-O(ℓ) bond. [209] In a subsequent publication these authors indicated that O-H cleavage may be kinetically favored due to much lower activation barrier compared to C-H cleavage, resulting in adsorbed species that agree with experimental observations.[210]

The concentration of methoxy on the surface thus determines the number of surface active sites on that surface. Based on C 1s photoemission the methoxy coverage on CeO₂(111) is 7 nm⁻² at 200 K. [208] The Ce cation density on CeO₂(111) is 7.9 nm⁻² therefore the methoxy coverage is ca. 0.9 ML. The methoxy coverage drops steadily as the sample is heated and methanol recombines and desorbs. The coverage is ca. 3 nm⁻² at 373 K. This is consistent with the methoxy coverage on ceria powder which was 4.2 $\mu\text{mole m}^{-2}$ at 100 °C which is equivalent to 2.5 nm⁻². [206] The methoxy coverage on CeO₂(100) is ca. 10 nm⁻² at 200 K. [205,211] On CeO₂(100) the density of bridge sites between Ce cations is 6.8 nm⁻² (Figure 7b). While the match is not perfect, the maximum methoxy coverage which occurs near 200 K on CeO₂(111) and CeO₂(100) is nearly 1 ML.

The TPD following methanol adsorption on CeO₂(111) and CeO₂(100) is shown in Figure 20. [205] On CeO₂(111) water and methanol are the primary products and they desorb between 200 K and 300 K (Figure 20, black lines). This demonstrates that even though the initial coverage of methoxy is high the methoxys and hydroxyls are unstable on this surface and recombine. It is important to note, however, that a competing reaction in this temperature range is the disproportionation of hydroxyls to produce water and a vacancy.

Where V_O is an oxygen vacancy. Isotopic labeling experiments with Ce¹⁸O₂(111) demonstrated that the water produced near 200 K contained lattice O. [208] The desorption of methanol between 200 K and 300 K is consistent with the decrease in methoxy coverage as the sample is annealed. The only reaction products at higher temperature result from the disproportionation of methoxy at ca. 560 K.

This suggests that $\text{CeO}_2(111)$ is primarily a redox type catalyst. Badlani and Wachs reached a similar conclusion on CeO_2 powder.[206] They also reported a similar decomposition temperature, 573 K. Methanol is an excellent reductant for $\text{CeO}_2(111)$ since the O:C ratio averaged over the products, CH_3OH , CH_2O and H_2O , is greater than O:C ratio in the reactant.

Methanol recombination and water formation are also evident on $\text{CeO}_2(100)$ (Figure 20, blue lines). The water desorption extends to a much higher temperature and does not spike as much near 200 K compared to $\text{CeO}_2(111)$. The methanol desorption behaves similarly. This demonstrates that methoxy and hydroxyl are both more stable on $\text{CeO}_2(100)$ than on $\text{CeO}_2(111)$. Methanol and formaldehyde desorption through methoxy disproportionation occur at the same temperature as on $\text{CeO}_2(111)$ but have a greater intensity, consistent with the significantly greater methoxy coverage on $\text{CeO}_2(100)$ at the reaction temperature.[211] CO , CO_2 , H_2 , and H_2O are also produced near 600 K. These products are indicative of a basic reaction mechanism.[206,212] The basic O anions on the surface dehydrogenate the methyl group in the methoxy.

When the ceria surfaces are reduced O-vacancies are created on the surface. On $\text{CeO}_{2-x}(111)$ this introduces three-fold adsorption sites between the Ce cations, equivalent to the sites occupied by the surface O in Figure 6, in addition to the on-top adsorption sites. Adsorption at these sites is much more stable as can be seen by the decrease of water and methanol desorption below 300 K on reduced $\text{CeO}_{2-x}(111)$ (Figure 21, black lines). This is also consistent with what was observed following water adsorption (compare Figure 11b and 12b, black lines) where reduction of the substrate attenuated the water desorption at low temperature. The methoxy is stable until about 660 K where it decomposes to produce CH_2O , CH_3OH , CO , H_2 and CO_2 . This demonstrates a transition from redox to basic behavior. The decomposition temperature shifts to higher temperature indicating a greater stability for the methoxy species. An important feature to note is the two peaks in the H_2 desorption. Isotopic labeling using CH_3OD demonstrated that the first peak at ca. 550 K resulted from the reaction between hydroxyls on the surface while the second peak resulted from the dehydrogenation of the methyl in the methoxy.[208] The desorption temperature due to hydroxyl recombination is consistent with what was observed when water was adsorbed on reduced $\text{CeO}_{2-x}(111)$ (Figure 12b).

The effect that reduction has on the reaction of methanol on $\text{CeO}_{2-x}(100)$ is not nearly as dramatic as the effect on $\text{CeO}_{2-x}(111)$. There is a slight decrease in the water and methanol desorption between 200 K and 500 K. There is also a small increase, ca. 25 K, in the CO and H_2

desorption temperature. The formaldehyde formation is greatly diminished, however. Ferrizz et al reported similar behavior for methanol adsorbed on oxidized and reduced $\text{CeO}_x(100)$ grown on YSZ(100).[83] Note that on $\text{CeO}_{2-x}(100)$ there is only a single H_2 desorption peak. Although isotopic labeling has not been performed presumably the hydroxyl reaction is similar to what was observed for water; specifically, the hydroxyls primarily react to form water and only a relatively small amount produce H_2 . Therefore the H_2 desorption peak mostly results from methoxy decomposition.

It's clear that O-vacancies increase the number of adsorption sites on the ceria surfaces, particularly on $\text{CeO}_{2-x}(111)$.[83,208] It has been argued, however, that O-vacancies are *necessary* for methanol adsorption and methoxy formation on $\text{CeO}_x(111)$.[12,83] Ferriz et al reported that less than 0.08 ML (0.6 nm^{-2}) adsorbed on fully oxidized single crystal $\text{CeO}_2(111)$ at 300 K.[83] It has also been observed by noncontact AFM that methoxy on $\text{CeO}_2(111)$ adsorbs in O-vacancy sites and methoxy in the on-top sites has not been observed.[113] Other experimental reports, as well as the results presented above, appear to indicate that methanol will adsorb and dissociate on the fully oxidized $\text{CeO}_2(111)$ surface.[50,208] There are several possible explanations for reconciling these observations. Calculations have shown that methoxy is weakly stable in the on-top site on $\text{CeO}_2(111)$.[207] This weak adsorption is consistent with the methanol desorption between 200 K and 300 K. As demonstrated by water adsorption on oxidized and reduced $\text{CeO}_x(111)$, hydroxyl adsorbed in a vacancy is relatively stable while hydroxyl adsorbed on top of a Ce cation is unstable.[15,51] This is evident from the water TPD spectra shown in Figure 11b. Likewise, based on calculations, methoxy is more stable in a vacancy compared to the on-top adsorption site.[207] If the methoxy and the hydroxyl were able to exchange adsorption sites following methanol adsorption at 180 K, as shown in (7), this would stabilize the methoxy and destabilize the hydroxyl.

This mechanism not only stabilizes the methoxy but also helps explain the water desorption at low temperature. This also places the methoxy in a vacancy site as observed by AFM. The removal of H through the desorption of water may also help to stabilize the methoxy regardless of its adsorption site. If the methoxy doesn't have a H to recombine with it will be stranded on the surface until it can decompose or react with another methoxy and

disproportionate at higher temperatures. It isn't clear why more activity wasn't observed by Ferriz et al.[83] The adsorption of methanol was conducted at 300 K by Ferriz et al but at 90 K by Mullins et al [208] and 110 K by Matolin et al [50]. Perhaps the weakly bound dissociative state recombines and desorbs too quickly to react with the surface at 300 K. It's also possible that the reactivity is different on the CeO₂(111) single crystal compared to the CeO₂(111) thin films although no obvious differences are evident in the STM and AFM images from these different surfaces.

Longer chain alcohols such as ethanol, 1-propanol and 2-propanol also adsorb on ceria surfaces by dissociating at the Ce / O acid-base pair sites. C 1s XPS indicates that the alkoxy coverage formed from the longer chain alcohols is the same as the methoxy coverage created by methanol adsorption.[205,213] This is consistent with what has been observed on powder samples where methanol, ethanol and propanol produce the same coverages.[214] The coverage is therefore determined by the interaction of the alcohol with the surface adsorption sites and not by adsorbate-adsorbate interactions.

The introduction of a C-C bond into the alcohol opens up new possibilities for the reaction products. The product distribution is again used to characterize the acidic or basic nature of the substrate.[214] Dehydration to produce alkenes and water (8) occurs on acidic / redox oxides and dehydrogenation to produce ketones or aldehydes (9) occurs on basic oxides. While ethanol, 1-propanol and 2-propanol follow similar reaction pathways, 2-propanol tends to produce the cleanest results following exclusively one pathway or the other on most oxides.[213,214]

We note, however, that these reaction descriptions are an oversimplification since they do not explicitly indicate how the O in the ceria may be involved. For example, on an oxidized surface the water from dehydration may incorporate O from the substrate followed by deoxygenation of the adsorbate to replenish the O in the substrate. The net reaction is dehydration as shown in (8) but the O in the H₂O does not come from the alcohol. Alternatively dehydration may lead to propylene as a product but, if the substrate is initially reduced, the O from the propoxide may re-oxidize the substrate and H₂ will be produced rather than H₂O.

The adsorption of 2-propanol at 180 K on oxidized $\text{CeO}_2(111)$ and $\text{CeO}_2(100)$ leads to water and alcohol desorption between 200 K and 450 K that is similar to what was observed for methanol (Figure 20).[205] On $\text{CeO}_2(111)$ water and 2-propanol desorb in a single, well-defined peak near 225 K. On $\text{CeO}_2(100)$ the low-temperature water and 2-propanol desorption is broad, extending to almost 500 K.

On $\text{CeO}_2(111)$ propylene is essentially the only hydrocarbon product and desorbs at 585 K.[205,213] There are trace amounts of acetone and 2-propanol desorbing between 500 K and 550 K. H is liberated when propoxy decomposes to propylene. This H desorbs as H_2 and does not react with the substrate to produce H_2O . This exemplifies the complex nature of this dehydration reaction as described above. Water is produced at 225 K from a reaction between the H in the alcohol and O in the substrate. The lattice O is replenished by the propoxy when it decomposes at 585 K. The net reaction is still predominantly dehydration. Because the O-balance between the reactant and products is effectively equal, 2-propanol is a poor reductant for $\text{CeO}_2(111)$.

Propylene is still the dominant product on $\text{CeO}_2(100)$ but a significant amount of acetone and 2-propanol are produced at 550 K as well.[205] As with methanol, the reaction behavior of 2-propanol indicates that $\text{CeO}_2(100)$ exhibits basic properties as well as redox character. Unlike methanol the decomposition of the propoxy intermediate leads exclusively to H_2O with no H_2 produced. In this case the surface is not O-starved since the propoxy can supply the O. We can surmise that the water that is produced between 200 K and 500 K results from a reaction between hydroxyls on the surface as in water and methanol, while the water produced near 585 K incorporates the H and O from the propoxy intermediate. C-C bond cleavage is also indicated as both CO and CO_2 are produced. 2-propanol acts as a reductant on $\text{CeO}_2(100)$ since although propylene is produced, O-rich products such as water, acetone, CO and CO_2 contain more O relative to C than the 2-propanol reactant.

Propylene is the only C-containing product, other than recombination to 2-propanol, following adsorption on reduced $\text{CeO}_{2-x}(111)$ and $\text{CeO}_{2-x}(100)$.[205,213] Here the substrate characteristics appear to differ from what was observed with methanol. The reaction of methanol indicated that reduction of the ceria appeared to make the surface more basic as the product distribution moved away from formaldehyde and toward CO. With 2-propanol the surface appears to be more acidic / redox as a) acetone is eliminated on $\text{CeO}_{2-x}(100)$ and b) the propylene product is produced at lower temperature on $\text{CeO}_{2-x}(111)$ than on $\text{CeO}_2(111)$. The primary difference between methanol and 2-propanol is likely the ability to break the C-O bond in 2-propanol. The branching between the ketone and the olefin reflects a competition between

cleaving the O-Ce bond and breaking the O-C bond. On the reduced surfaces O-C bond cleavage is clearly favored. In methanol C-O cleavage may occur by C-C coupling, methane formation or CH_x radical ejection. No products from any of these pathways were detected from either $\text{CeO}_{2-x}(111)$ or $\text{CeO}_{2-x}(100)$, although these products have been observed from other oxide surfaces.[11] Interestingly, the H from the 2-propanol decomposition was again incorporated in H_2 on $\text{CeO}_{2-x}(111)$ and H_2O on $\text{CeO}_{2-x}(100)$. As a result 2-propanol acts as an oxidant on $\text{CeO}_{2-x}(111)$ but has no effect on the oxidation state of $\text{CeO}_{2-x}(100)$.

The adsorption and reaction of the C_2 -diol, ethylene glycol, was studied on oxidized and reduced $\text{CeO}_x(111)$.[215] As with the mono-alcohols this diol reacts with the surface by cleaving an O-H bond producing an alkoxy and a hydroxyl on the surface. O 1s photoemission indicated that at 190 K the molecule initially adsorbed through only one of the alcohol groups, i.e. alkoxy and alcohol were evident in the photoemission spectrum. Also in a manner similar to the mono-alcohols, glycol recombination and water desorption occurred as the sample was heated to 250 K. O vacancies and adsorption sites that were created upon annealing enabled dissociation and adsorption of the alcohol at the other end of the molecule creating adsorbed ethylenedioxy, $-\text{OCH}_2\text{CH}_2\text{O}-$. On the oxidized $\text{CeO}_2(111)$ surface this intermediate followed two reaction pathways; C-O bond cleavage and rearrangement resulting in acetaldehyde desorption, and C-C bond cleavage to produce adsorbed formate. The formate ultimately decomposed to produce water and CO. On reduced $\text{CeO}_{2-x}(111)$ the ethylenedioxy intermediate also underwent C-O bond cleavage to produce acetaldehyde but also produced a stable enolate, $-\text{O}-\text{CH}=\text{CH}_2$. This species underwent further C-O bond cleavage to produce ethylene and acetylene in a manner similar to the adsorption and reaction of acetaldehyde on reduced $\text{CeO}_{2-x}(111)$ (see section 5.2.1.3).[216]

Ceria powders are known to selectively produce unsaturated alcohols from larger diols such as 1,3-propanediol and 1,3-butanediol.[217] This would result from the dehydration at one end of the diol leaving the alcohol at the other end intact. However, a computational analysis of the reaction of 1,3-butanediol on $\text{CeO}_x(111)$ using density functional theory produced an entirely different reaction model compared to those discussed above.[218,219] In this model the $-\text{OH}$ groups interact with the surface without dissociation while a H on the methylene in the 2-position was abstracted by the substrate. The reaction was completed by the cleavage of an $-\text{OH}$ from the intermediate producing water and an unsaturated alcohol. To our knowledge this mechanism has not been substantiated by experimental observations.

5.2.1.2 - Carboxylic Acids

The adsorption and reaction of carboxylic acids has also been used as a probe of acid – base properties on oxides.[6] As with the alcohols, the acids easily deprotonate to form carboxylate upon adsorption. Dehydration products are favored on acidic substrates while dehydrogenation occurs on basic substrates. The products for these two reaction pathways are very clear for formic acid where dehydration leads to CO plus water while dehydrogenation produces CO₂ and H₂. For acetic acid dehydration leads to ketene, CH₂=C=O. Dehydrogenation leads to total decomposition products such as CO₂ and CO.

Formic acid adsorption and reaction has been studied on CeO₂(111) [62,71,75,78] and on CeO₂(100).[75] Formic acid formed a more stable adsorbed species on CeO₂(111) than methanol. This was ascribed to the increased acidity of formic acid compared to methanol. On the basis of C 1s XPS, C k-edge NEXAFS and vibrational spectroscopy it was determined that formic acid dissociated into formate and H depositing the proton on a surface O forming a hydroxyl. The splitting between the symmetric and asymmetric O-C-O stretching frequencies, $\nu_s(\text{OCO})$ and $\nu_a(\text{OCO})$, in the vibrational spectra of the adsorbed formate have been used to determine the nature of the formate adsorption site.[220-222] A small value for the splitting, e.g. less than 200 cm⁻¹, was attributed to a bidentate configuration whereas a splitting significantly greater than 200 cm⁻¹ was attributed to a monodentate configuration. The vibrational frequencies reported for formate on CeO₂(111) are in general agreement however the splitting between $\nu_s(\text{OCO})$ and $\nu_a(\text{OCO})$ fall into a “gray area” with values of 220 cm⁻¹ [75], 217 cm⁻¹ – 232 cm⁻¹ [78] and 196 cm⁻¹ – 275 cm⁻¹ [62]. Gordon et al noted that in addition to the adsorbate bonding geometry the splitting could also be influenced by co-adsorbed H and the detailed nature of the adsorption site. [78] On the basis of DFT calculations and surface selection rules, they argued that the formate adsorbed in a bidentate configuration.

The reaction products following formic acid adsorption on oxidized and reduced CeO_x(111) are shown in Figure 22 (a) and (c). [62] All of the studies that reported TPD results for formic acid on CeO₂(111) have qualitatively agreed; the principal product is CO along with CO₂ and water with a small amount of formaldehyde.[62,71,75] Senanayake et al and Lykhach et al also reported desorption of H₂ with the latter additionally observing methane. The details are quite different between the various studies, however. Stubenrauch et al reported that all of the products desorbed at nearly same temperature in a single symmetric peak near 610 K. [75] Lykhach et al reported much more complex desorption spectra, as shown in Figure 22 (a), and a slightly lower nominal decomposition temperature. [62] The desorption spectra reported by Senanayake and Mullins clearly divided the decomposition into two regions; CO₂ and H₂ near 350 K and CO above 400 K. [71] In addition, they noted a water desorption peak near 300 K as

did Lykhach et al. By using isotopically labeled $\text{Ce}^{18}\text{O}_2(111)$ Senanayake and Mullins determined that the water at 300 K resulted from the disproportionation of surface hydroxyls. When methanol is adsorbed on $\text{CeO}_2(111)$ this reaction occurs near 220 K.[208] On the basis of DFT calculations Gordon et al determined that $-\text{OH}$ is stabilized when located near co-adsorbed formate on $\text{CeO}_2(111)$. [78]

On reduced $\text{CeO}_{2-x}(111)$ the decomposition of formate results in more CO and H_2 and a significant decrease in CO_2 (Figure 22 (c)). [62,71] As with methanol, this indicates that reduced $\text{CeO}_{2-x}(111)$ is more basic than oxidized $\text{CeO}_2(111)$, and that the reduced surface competes with the desorption products for O .

Stubenrauch et al determined that formic acid behaved largely the same on $\text{CeO}_2(100)$ compared to $\text{CeO}_2(111)$. The CO / CO_2 product ratio was slightly greater on $\text{CeO}_2(100)$ as was the formate decomposition temperature.

Acetic acid also dissociates and adsorbs as acetate and hydroxyl on $\text{CeO}_2(111)$ and $\text{CeO}_2(100)$, [75] [205] and the carboxylate coverage is similar to what was obtained from formic acid. The TPD from acetic acid on oxidized and reduced $\text{CeO}_x(111)$ and $\text{CeO}_x(100)$ is shown in Figure 23 (A) and (B), respectively. On $\text{CeO}_2(111)$ (Figure 23 (A), black lines) the primary reaction products are ketene, water, CO and CO_2 . This result is very consistent with what was reported by Stubenrauch et al on $\text{CeO}_2(111)$ [75] and indicates a mixture of dehydration / acidic and dehydrogenation / basic behavior. The water desorption peak near 300 K is similar to what was observed with formic acid and suggests stabilization of the surface $-\text{OH}$ by the co-adsorbed acetate. In addition to these principal products there are several minor products such as acetone, acetylene and the recombination of $-\text{OH}$ plus acetate to produce acetic acid at ca. 500 K. Acetone is the result of the ketonization reaction which in addition to acetone produces CO_2 plus water. It has been suggested that this reaction requires two acetates bound to the same metal cation.[6] Presumably this can only occur at defect sites on fully oxidized $\text{CeO}_2(111)$ which may explain why it is only a minor product.

On $\text{CeO}_2(100)$ (Figure 23(A), blue lines) the ketene production is dramatically decreased while the CO_2 formation is increased compared to $\text{CeO}_2(111)$. This is consistent with what was observed for 2-propanol where the dehydration pathway is less favored on the (100) surface. Stubenrauch et al also studied acetic acid on $\text{CeO}_2(100)$ and reported very different results.[75] They found that ketene formation was essentially the same as on $\text{CeO}_2(111)$ except for an increase in desorption temperature. They also report that formic acid produced a higher CO / CO_2 product ratio on $\text{CeO}_2(100)$ than on $\text{CeO}_2(111)$, indicating that the $\text{CeO}_2(100)$ surface is less basic than $\text{CeO}_2(111)$.

Reduction of the ceria surfaces has a dramatic effect as shown in Figure 23(B). The intensity of the C-containing products is greatly diminished with only small amounts of CO, CO₂, ketene and acetylene evident. Note that although reduction presumably increases the number of multiply-under-coordinated cation sites on both surfaces, acetone formation is largely eliminated. This is because re-oxidation of the reduced ceria inhibits competing reaction pathways where the products contain O.

XPS indicates that more than 50% of the C from the acetic acid is left on the surface as graphitic-like C after TPD to 800 K. This is perhaps surprising since the O content in the acetic acid is higher than that in ethanol or 2-propanol which react cleanly on the reduced surfaces. Acetic acid produces very stable surface species that remain on the surface until they dehydrogenate to produce H₂ and H₂O on CeO_{2-x}(111) and CeO_{2-x}(100), respectively and deoxygenate to re-oxidized the substrate. This leaves the remaining C fragments few options to desorb as stable products.

5.2.1.3 – Aldehydes, Ketones and Ethers

Aldehydes, ketones and ethers represent a different class of adsorbates compared to alcohols and carboxylic acids. They cannot deprotonate and attach to acid-base sites on the surface as a Brønsted acid as is the case with alcohols and carboxylic acids. They can act as a Lewis base with the lone-pair electrons on the O interacting with cationic Lewis acid sites or they can break a C-O bond so that the C can react with a surface O. The interaction of formaldehyde,[223] acetaldehyde[216], acetone,[224], dimethylether and diethylether[225] with stoichiometric CeO₂(111) is weak. The parent molecules desorb molecularly between 200 K and 225 K. The TPD for acetaldehyde on CeO₂(111) is shown by the black lines in Figure 24.

Acetaldehyde adsorption on CeO₂(100) is much stronger than on CeO₂(111).[61] The acetaldehyde desorption extends from 200 K to above 400 K. In addition to the parent molecule, above 400 K additional products are observed. Total decomposition to CO, CO₂ and H₂O is the principal pathway with a small amount of dehydration to produce acetylene at 700 K. In addition a notable product is the small amount of crotonaldehyde that is evident at 430 K. This is the result of the aldol condensation coupling reaction between two acetaldehyde molecules.[6] The adsorption and reaction on CeO₂(100) is consistent with trends previously observed for the other oxygenates. Specifically, stronger adsorption results from a greater number of coordination vacancies around the Ce cation on CeO₂(100) compared to CeO₂(111). The CO and CO₂ products result from dehydrogenation of the adsorbed acetaldehyde by the basic O

anions. The water desorption results from the relative ease with which the H reacts with the surface O.

Introduction of surface vacancies in reduced $\text{CeO}_{2-x}(111)$ has a dramatic effect on the adsorption and reaction of formaldehyde,[223] acetaldehyde[216] and acetone[224]. These carbonyl-containing molecules now adsorb strongly on the $\text{CeO}_{2-x}(111)$ surface. In addition to desorbing non-dissociatively, formaldehyde decomposes into CO and H_2 . As dioxymethylene (see below) is heated on reduced $\text{CeO}_{2-x}(111)$ it disproportionates into methoxy and formate. [223] These surface species then go on to react in the same manner as if they had been formed from methanol[208] and formic acid.[71] They decompose into formaldehyde, CO and H_2 .

Acetaldehyde produces ethylene, acetylene and H_2 on $\text{CeO}_{2-x}(111)$ (Figure 24, blue lines). The desorption of the parent molecule also changes. The low temperature desorption near 220 K is suppressed and two new peaks appear near 400 K and between 500 K and 650 K.[216] In a similar manner, acetone desorbs as molecular acetone near 500 K and also decomposes into propyne, H_2 and CO.[224]

Acetaldehyde adsorbed on reduced $\text{CeO}_{2-x}(100)$ desorbs from 200 K to 600 K with no significant new peaks as on $\text{CeO}_{2-x}(111)$. [61] CO, CO_2 and crotonaldehyde formation are eliminated and H_2 desorption replaces H_2O . Ethylene is produced at about the same temperature as on $\text{CeO}_{2-x}(111)$. XPS indicates that almost 40% of the C in the adsorbed acetaldehyde remains on the $\text{CeO}_{2-x}(100)$ surface as graphitic-like C at 800 K.

The adsorption states and reactions pathways for these carbonyl-containing molecules on ceria surfaces are complex. As shown below for acetone, the molecule can adsorb non-dissociatively on oxide surfaces either through the O lone as an η^1 – monoxy species (a) or react with a surface O to create an η^2 – dioxy species (b).[226]

These two species are indistinguishable in C 1s XPS.[216,223,224] However they can be differentiated in C k-edge NEXAFS based on the presence or absence of the $\text{C}=\text{O}$ π^* resonance. It was determined that formaldehyde adsorbs on oxidized $\text{CeO}_2(111)$ as η^2 – dioxymethylene due to the absence of the $\text{C}=\text{O}$ π^* resonance. [223] DFT calculations found a similar result.[227] However, acetaldehyde and acetone both adsorbed in the η^1 – monoxy

configuration. [216,224] Vibrational spectroscopy and DFT calculations confirmed this result for acetaldehyde.[77] On reduced $\text{CeO}_{2-x}(111)$ these compounds all adsorb as η^2 – dioxy.

In addition to the inability to differentiate between the η^1 – carbonyl species and the η^2 – dioxy species in the C 1s spectra, it was observed that the carbonyl compounds were sensitive to x-ray induced dissociation whereby H was ejected and surface carboxylates were produced. Therefore, when using XPS to analyze carbonyl-containing oxygenates on ceria surfaces care must be exercised to limit x-ray exposure. Possible x-ray damage must be tested by varying x-ray exposure and analyzing various sample positions.[216,223,224]

The reaction pathway for acetaldehyde and acetone on reduced $\text{CeO}_{2-x}(111)$ is different from that of formaldehyde. These molecules dehydrogenate to form an enolate as shown below for acetaldehyde.

Figure 25 shows two spectroscopic pieces of evidence for this transformation. In the C 1s XPS there is a shift from a binding energy indicative of two C-O bonds, i.e. carbonyl or dioxy, to a position indicative of a single C-O bond, i.e. alkoxy. The peak at 284.8 eV in the C k-edge NEXAFS spectrum at 450 K is indicative of a C=C double bond. Note that the peaks at 284.8 eV and 286.5 eV are both related to the C=C bond. The peak at lower photon energy is at the =CH₂ end while the peak at higher photon energy is at the OCH= end.[228] FTIR and DFT calculations confirm this result.[77] The enolate is also formed on oxidized and reduced $\text{CeO}_x(100)$. [61] On reduced $\text{CeO}_{2-x}(111)$ re-hydrogenation of the enolate above 400 K leads to acetaldehyde desorption. C-O bond cleavage along with hydrogenation at the carbonyl C produces ethylene while additional dehydrogenation leads to acetylene. On $\text{CeO}_x(100)$ further dehydrogenation and C-C bond cleavage also occurs leading to CO, CO₂ and C deposited on the surface.

Vibrational spectroscopy and DFT calculations have shed additional light on the first acetaldehyde desorption peak near 400 K on $\text{CeO}_{2-x}(111)$ (Figure 24, blue line). [77] This desorption feature results from the decomposition of a dimer formed from the coupling of the carbonyl O and the acyl C of two acetaldehyde molecules.

As noted at the beginning of this section, dimethyl ether and diethyl ether interact weakly and do not decompose on either oxidized or reduced $\text{CeO}_x(111)$. [225] Co-adsorption of diethyl ether with $-\text{OH}$ on reduced $\text{CeO}_{2-x}(111)$ resulted in decomposition of the ether into ethoxy and formate. A similar decomposition did not occur for dimethyl ether suggesting that dissociation of the C-O bond requires the presence of β -hydrogen.

5.2.2 – Other organic molecules

5.2.2.1 – Methanethiol

Methanethiol, CH_3SH , is the S-containing analog of methanol, CH_3OH . The C and S coverage at 150 K on oxidized $\text{CeO}_2(111)$ is similar to the C and adsorbate O coverage following methanol exposure. [229] However, whereas methanol almost totally decomposes into methoxy and $-\text{OH}$ below 200 K, only 40% of the thiol decomposes into $\text{CH}_3\text{S}-$ plus $-\text{OH}$. More than 90% of the chemisorbed thiol desorbs molecularly below 300 K. The remainder produces a small amount of methane leaving S on the surface. This decomposition of the thiol was attributed to reaction at step sites and defects.

Adsorption of methanethiol on reduced $\text{CeO}_{1.75}(111)$ was more similar to methanol compared to the fully oxidized surface in that it dissociated almost exclusively into $\text{CH}_3\text{S}-$ plus $-\text{OH}$ below 200 K. The thiolate and hydroxyl were relatively stable with only a small amount of recombination to produce methanethiol below 300 K. The major reaction product was methane at 600 K along with small amounts of CH_3SH , CH_2O and H_2O . Unlike the decomposition of CH_3OH on reduced $\text{CeO}_{2-x}(111)$, H_2 was largely absent from the products. As with the reaction of H_2S [200] and SO_2 [191] on reduced $\text{CeO}_{2-x}(111)$, the decomposition of methanethiol left a considerable amount of S on the surface. This sulfur diffused into the bulk above 800 K rather than desorbing in S-containing products.

5.2.2.3 – Dimethyl methylphosphonate

Dimethyl methylphosphonate (DMMP, $(\text{CH}_3\text{O})_2\text{PO}(\text{CH}_3)$) is frequently used as a simulant molecule for organophosphorous nerve agents because DMMP is nontoxic but has structural similarities to the nerve agents. DMMP readily adsorbs and reacts on oxidized and reduced $\text{CeO}_x(111)$. The reaction pathway has been determined through a combination of TPD, sXPS and FTIR. [230] As shown in Figure 26, DMMP initially adsorbs at 200 K through the lone pair electrons on the O in a manner similar to acetaldehyde and acetone. As the sample is heated a P-O bond is cleaved to one of the methoxy groups forming methoxy methylphosphonate (MMP)

and methoxy on the surface. The bonding of the MMP intermediate appears to be more analogous to a carboxylate than it does to an η^2 – dioxy. As the methoxy species decompose the reaction products resemble those from methanol adsorption on $\text{CeO}_2(111)$ [208] with CH_3OH and CH_2O desorbing between 400 K and 500 K. The other methoxy group eventually cleaves from the MMP and reacts on the surface leaving methylphosphonate (MP). The C-P bond is tenacious and doesn't break until above 700 K where it also reacts with the surface to produce formaldehyde and water. The formation of CH_3OH , CH_2O and H_2O results in the reduction of the ceria. PO_x species remain on the surface even up to 900 K and decrease the ability of the $\text{CeO}_x(111)$ surface to react with DMMP in subsequent adsorption / reaction cycles. However, some activity remains even up to seven adsorption cycles.

The adsorption and reaction of DMMP on reduced $\text{CeO}_{2-x}(111)$ follows a similar pathway with progressive cleavage of methoxy groups and eventual cleavage of the methyl group. As with methanol, reduced $\text{CeO}_{2-x}(111)$ shifts the reaction products toward CO and H_2 formation as the surface becomes more effective at dehydrogenating the adsorbed species.

6 – Metal particles supported on ceria surfaces

This section will first consider the structure of metal particles on ceria surfaces. To date the only experimental studies have been conducted on $\text{CeO}_2(111)$ surfaces although there have been some computational studies on other surfaces.

This section will then be followed by a discussion of the reactions of various molecules on these metal loaded surfaces. As in Section 5 the discussion will be divided by different molecules or classes of molecules rather than by the type of metal.

6.1 – Structure of metals on ceria surfaces

Metal atoms and clusters display both relatively weak interactions with ceria surfaces but also strong interactions in some cases; up to and including the formation of mixed metal oxides with the ceria substrate. Figures 27 and 28 show examples of weak and strong interactions, respectively. Figure 27 shows an STM image of Au deposited on $\text{CeO}_2(111)$ at 300 K.[231] The Au particles nucleate at step edges and defect sites on the oxidized surface. Alternatively in Figure 28 Ni clusters are shown decorating the $\text{CeO}_2(111)$ terraces with no significant preference for the step edges.[232] Ag[233,234], Au[37,235] and Rh[34] have been reported to adsorb primarily at step edges and defects. It was noted that Rh decorates the edges at low coverages but populates the terraces more uniformly at high coverages. Au adsorbs on the terraces, with no preference for edges and defects, when deposited at 10 K.[236] Ni[232,237]

and Pt[238] cover the $\text{CeO}_2(111)$ terraces uniformly. Zhou et al reported that Pd had a partial preference for decorating step edges on fully oxidized $\text{CeO}_2(111)$ [34,173] whereas Wilson and co-workers indicated that Pd nanoparticles uniformly covered the terraces on partially reduced $\text{CeO}_{2-x}(111)$. [239] Finally, Al[240], Ga[241], Mg[181], Sn[55], Ti[242], V[243] and W[244] are all either heavily oxidized by the O in the ceria or formed mixed metal oxides with the ceria substrate.

There have been more DFT calculations reporting the adsorption of metals on $\text{CeO}_2(111)$ and $\text{CeO}_2(110)$ than there have been experimental observations. Adsorption sites, energies and charge transfer behavior have been reported for Ag[233,245-247], Au[245-253], Cu[245-247,254-256], Ni[254], Pd[239,257-259], Pt[258,260-262] and Rh[258,259,263]. The adsorption of single metal atoms has generally found an affinity between the admetal and surface O with a preference for adsorption in the $\text{CeO}_2(111)$ or $\text{CeO}_2(110)$ O-O bridge site, and occasionally the O three-fold hollow site on $\text{CeO}_2(111)$ or the O a-top site. Adsorption in a hollow site above a second layer Ce cation has been energetically unfavorable. In a few cases clusters of metal atoms have been studied. In most cases the clusters form three dimensional structures that maximize the metal-metal bonds. The trend is that while metal to surface interactions are favorable, metal-metal interactions are more energetically stable. This was demonstrated in the microcalorimetry work of Farmer et al where they observed that the heat of adsorption for Ag on $\text{CeO}_{2-x}(111)$ was initially near 200 kJ/mole and grew to 285 kJ/mole at high coverage.[234] They noted, however, that the initial heat of adsorption for Ag on $\text{CeO}_{2-x}(111)$ was greater than that for Ag on $\text{MgO}(100)$ [264,265] indicating a stronger metal-surface interaction.

In general, calculations have determined that there is an electron transfer from the adsorbed metal atoms/particles to the ceria surface resulting in a small positive charge on the admetal and a reduction of the Ce^{4+} cations. Experimentally reduction of the Ce has been reported in the Ce 3d, Ce 4d and Ce 4f photoemission following metal adsorption.[54,233-235,237-239,260,266-270]. Despite an indication of a reduction of the Ce, oxidation of the admetal has generally not been observed except in cases of O transfer from the substrate to the admetal or where mixed metal oxide formation occurs between the admetal and the ceria. Small positive binding energy shifts relative to the bulk metal peak position have been attributed to final state effects associated with small metal particles.[271]

Strong metal-support interaction (SMSI), i.e. encapsulation of the metal nanoparticle by the ceria substrate, was reported for Pt on reduced $\text{CeO}_{2-x}(111)$. [172] This occurred when Pt on reduced $\text{CeO}_{2-x}(111)$ was annealed to 900 K in vacuum as indicated by a decrease in the Pt 4f

XPS intensity and poisoning of subsequent CO adsorption due to the encapsulation. The SMSI effect was reversed following oxidation at 600 K.

6.2 – Adsorption / Reaction on metals supported on ceria surfaces

6.2.1 – CO

Two aspects of the interaction of CO with metals supported on cerium oxides surfaces have been studied; the standard UHV adsorption/desorption phenomena as measured by XPS, vibrational spectroscopy and TPD, and reaction behavior, specifically CO oxidation and the water-gas shift reaction. The WGS reaction will be considered in Section 6.2.3.

On fully oxidized CeO_2 the adsorption and desorption of CO largely resembles what has been observed on pure, unsupported metals or metals supported on less reactive oxide substrates such as SiO_2 or Al_2O_3 , i.e. the ceria substrate has little effect on the adsorption/desorption of CO. This is true on Au[272], Pd[173,272-274], Pt[121,172,275] and Rh[76,170,171,276-279]. One major difference for some of these metals supported on CeO_2 compared to the unsupported metals is the production of CO_2 during TPD from Pt[172,275] and Rh[170,171,276-278]. The CO_2 was produced by CO reacting with O from the ceria. Isotopic labeling also indicated that in some cases the CO adsorbed on the metal particles exchanged O with the ceria substrate without necessarily reacting to form CO_2 . [171-173] The CO_2 formation was face-specific. Rh on $\text{CeO}_2(111)$ produced CO_2 whereas Rh on $\text{CeO}_2(100)$ did not.[171] Further, the ability of the ceria substrate to donate O to the CO was inhibited by annealing the ceria to elevated temperatures.[277,278]

The participation of the O from the ceria substrate was also demonstrated in CO oxidation reactions on Pd[280,281], Pt[280,282] and Rh[276,277]. On pure metal surfaces the CO oxidation rate is inversely related to the CO pressure as CO adsorption poisons the O adsorption sites on the metal. In the presence of the ceria substrate however, a second CO mechanism is evident where the rate is zero-order in CO pressure. This is attributed to CO reacting with O in the substrate. CO oxidation on Au nanoclusters on $\text{CeO}_2(111)$ has also been examined by DFT. On fully oxidized stepped- $\text{CeO}_2(111)$ Kim and Henkelman determined that O in the ceria at the step edges reacted favorably with CO adsorbed on the Au.[283] The same authors also studied CO oxidation over Au on partially reduced $\text{CeO}_{2-x}(111)$. [284] In that study they determined that O_2 adsorbed at the interface between the Au nanoparticle and an O-vacancy in the ceria led to a favorable pathway for oxidation.

A dramatic effect was observed when CO was adsorbed on Rh supported on reduced $\text{CeO}_{2-x}(111)$. The CO dissociated into C and O. As shown in Figure 29 a new, high temperature

CO desorption state appears in the TPD of CO/Rh/CeO_{2-x}(111).[76] The isotopic labeling indicates that the high temperature CO state contained O obtained from the CeO_{2-x}(111) substrate. The C 1s core level sXPS, Figure 30, shows that the CO decomposes between 300 K and 500 K on Rh / CeO_{2-x}(111).[279] CO decomposition has also been observed on highly stepped vicinal Rh(331), Rh(755)[285] and Rh(210)[286] and on Rh particles on thin film Al₂O₃. [287,288] In those cases the decomposition was related to the Rh structure and was promoted at under-coordinated edge sites. For Rh on reduced CeO_{2-x}(111) the degree of decomposition was not related to the Rh coverage or particle size but was directly correlated to the degree of ceria reduction.[279] The most likely explanation is that the CO dissociation is activated at the Rh-ceria interface and is related to O-vacancies in the ceria.

Small amounts of CO dissociation were also observed on Pd[173] and Pt[172] on reduced CeO_{2-x}(111) but the degree of dissociation was less than 10%. Other types of metal-support interactions were evident for CO adsorbed on Pt/CeO_{2-x}(111).[172] As noted above, when Pt/CeO_{2-x}(111) was annealed above 900 K the Pt became encapsulated by the ceria and all CO adsorption was suppressed. On Pt/CeO_{2-x}(111) samples that were not annealed to high temperatures there were low temperature CO desorption states observed between 180 K and 220 K. A possible explanation is that the CO is adsorbed as a carbonyl on very small Pt particles. Low temperature CO desorption was also observed from small Pd particles on Al₂O₃. [289] This low temperature CO desorption was attributed to the decomposition of Pd-carbonyl species. Low temperature CO desorption also occurred when CO was co-adsorbed with O₂ on Rh/CeO₂(111).[290] It was proposed the CO+O dispersed the Rh clusters and produced Rh – gem-dicarbonyl species on the surface. An alternative explanation for the low temperature desorption of CO on Pt/CeO_{2-x}(111) is electron transfer from Ce³⁺ to the Pt. It has been shown on Pt/TiO₂ that dopants in the titania can weaken the CO-Pt adsorption strength through electron transfer to the Pt.[291]

6.2.2 – NO

NO adsorption and decomposition was studied on Pd, Pt and Rh on CeO₂ surfaces. In the absence of an oxide support NO has been shown to adsorb both molecularly and dissociatively on all three metals. However the degree of dissociation, and hence the propensity to recombine and desorb as N₂, has been found to be highly structure sensitive. NO produces little or no N₂ on the low index Pd(111), Pd(100) and Pd(110) surfaces.[292,293] NO adsorption on the more highly stepped Pd(311) produces considerable N₂ however.[293] NO produces no N₂ on Pt(111), a small amount on Pt(110) and nearly 50% of the adsorbed NO produces N₂ on

Pt(100).[294] On Pt(410) over 90% of the NO decomposes. NO on Rh is somewhat more complex in that all faces of Rh are highly active for NO decomposition. However, the temperature at which NO decomposes is lower on Rh(100) than on Rh(111).[295] The dissociation of NO on Rh surfaces is self-poisoning. The degree of dissociation decreases as the NO coverage increases. Multiple sites are necessary for NO decomposition and these can be blocked by other NO molecules or by decomposition products.

NO decomposition was studied on Pd[147] and Pt[121] supported on amorphous CeO_2 films. NO on Pd/ CeO_2 produced predominantly N_2 . The authors compared this to Pd/ Al_2O_3 where the NO mostly desorbed molecularly. The differences in behavior between Pd/ CeO_2 and Pd/ Al_2O_3 are not entirely clear however the results on Pd single crystals suggests that there may be a morphological difference between the Pd particles on the two oxide surfaces. If the ceria was reduced prior to NO adsorption the resulting TPD spectrum was qualitatively similar to that which results from Pd on oxidized ceria with respect to desorption temperatures and product distribution. However the overall intensity increased suggesting that the NO adsorbed on the reduced ceria as well as on the Pd but ultimately reacted on the Pd. NO adsorption on Pt/ CeO_2 resulted in predominantly N_2 desorption.[121] Unlike Pd, the results for Pt/ CeO_2 were similar to those for Pt/ Al_2O_3 . [296] This suggests that the Pt morphology was similar on the two oxides. The authors suggest that the propensity for NO decomposition was related to the particulate nature of the Pt particles compared to the flat, single crystal surfaces.

The desorption of N_2 and NO from NO/Rh/ $\text{CeO}_2(111)$ [297] resembles that from NO/Rh(111).[298] This indicates that there is little interaction between the Rh and the $\text{CeO}_2(111)$ substrate. However reduction of the ceria substrate increases the amount of N_2 that desorbs and totally suppresses the NO desorption for degrees of reduction greater than 40% Ce^{3+} ($\text{CeO}_{1.8}(111)$). Further, at any given temperature from 250 K to 350 K the degree of dissociation of NO on the Rh particles, as measured by N 1s sXPS, was greater on reduced $\text{CeO}_{2-x}(111)$ than on oxidized $\text{CeO}_2(111)$. [297] Overbury et al suggested three possible mechanisms for the enhanced NO dissociation on Rh/ $\text{CeO}_{2-x}(111)$; i) electron transfer from Ce^{3+} to Rh, ii) O spillover from the Rh to the reduced ceria, and iii) morphological differences between the Rh particles on the oxidized and the reduced ceria. RPES experiments indicate that the Ce^{3+} concentration increases, rather than decreases, following Rh deposition, even on initially partially reduced $\text{CeO}_{2-x}(111)$, however the effect is greater on initially oxidized ceria.[269] Therefore electron transfer to the Rh is unlikely the cause of enhanced dissociation on Rh/ $\text{CeO}_{2-x}(111)$.

Since NO dissociation on Rh is self-inhibiting, spillover of O from the Rh surface to CeO_{2-x} would remove O from the Rh and would conceivably eliminate the inhibiting effect of the O. Two observations eliminated this possibility, however. When the NO coverage was reduced to 35% of its saturation coverage on the Rh particles the NO dissociation was still greater on $\text{Rh/CeO}_{2-x}(111)$ than on $\text{Rh/CeO}_2(111)$. [299] On $\text{Rh}(111)$ it was shown that at reduced NO coverage the inhibition effect disappeared. [298] Further, in another experiment, $\text{Rh/CeO}_{2-x}(111)$ was exposed to H_2O which dissociated on the ceria surface filling the O vacancies. The NO dissociation on the hydroxylated $\text{Rh/CeO}_{2-x}(111)$ was the same as on the hydroxyl-free surface indicating the O vacancies on the ceria did not enhance dissociation. [299]

STM measurements indicate similar growth of Rh particles on oxidized and reduced surfaces. [34] These measurements did not provide atomic level information however, so it isn't known what surface planes are exposed, or whether the particles have a different degree of step and kink sites, on a reduced surface compared to the oxidized surface. Since NO dissociation is greater on $\text{Rh}(110)$ [300] and $\text{Rh}(100)$ [301] than on $\text{Rh}(111)$ [298] it's possible that atomic level morphological differences are responsible for the enhanced dissociation on $\text{Rh/CeO}_{2-x}(111)$.

NO was also co-adsorbed with CO [302] or C_2H_4 [201] on $\text{Rh/CeO}_x(111)$. These co-adsorbates are particularly relevant in relation to the reduction of NO_x in automotive exhaust. The reaction between CO and NO on Rh has been studied by a number of authors [303-308] and the broader literature has been reviewed by Zhdanov and Kasemo. [309] When CO and NO are co-adsorbed on $\text{Rh/CeO}_2(111)$ the interaction is as has been observed on the Rh metal surfaces. [302] CO reacts with O from the dissociated NO to produce CO_2 and the N atoms combine to produce N_2 . The only surface species observed are CO, NO, N and O. When CO and NO are co-adsorbed on reduced $\text{Rh/CeO}_{2-x}(111)$ new reaction pathways are observed. These new pathways result from a) the depletion of O on the Rh due to spillover of O from Rh to $\text{CeO}_{2-x}(111)$ following NO dissociation and b) the dissociation of CO on reduced $\text{Rh/CeO}_{2-x}(111)$ at elevated temperatures (see Sec. 6.2.1). The depletion of O on the Rh leads to the formation of OCN through the reaction of $\text{CO} + \text{N}$. The OCN decomposes into gas phase $\text{CO} + \text{N}_2$. The dissociation of CO into $\text{C} + \text{O}$ leads to the formation of C_xN_y fragments on the Rh particles. These eventually decompose at high temperatures leading to N_2 and CO through the reaction of C on the Rh and O in the ceria. Notably no CO_2 is produced from $\text{CO} + \text{NO}$ on $\text{Rh/CeO}_{2-x}(111)$. The re-oxidation of the ceria inhibits the reaction between CO and O on the Rh.

$\text{C}_2\text{H}_4 + \text{NO}$ have also been investigated on $\text{Rh/CeO}_x(111)$. [201] As discussed in Section 6.2.6, the C_2H_4 decomposes to produce C + H on the Rh. These react to produce H_2 , through

reaction between the H, and CO, through C reaction with the ceria. The H does not react with the ceria to form water.[170,201] van Hardeveld et al studied the reaction between C₂H₄ and NO on Rh(111).[310] Individually C₂H₄ and NO produce C and H₂, or NO and N₂, respectively. Reactions between C₂H₄ and NO produced H₂O, CO, CO₂ and HCN. The same products were observed on Rh/CeO₂(111) except there was no H₂ or HCN. In comparison with the reaction of C₂H₄ by itself on Rh/CeO₂(111), it is clear that the H₂O and CO₂ result from a reaction between C₂H₄ and the O from the NO on the Rh nanoparticles. The absence of H₂ apparently resulted from the relative coverage of C₂H₄ and NO so that all of the H was consumed by the O from the NO. No C_xN_y intermediates were detected on the Rh. The C was more reactive with O on the Rh and O in the ceria than it was with N. The absence of C_xN_y intermediates resulted in no HCN products. When C₂H₄ and NO were co-adsorbed on reduced Rh/CeO_{2-x}(111) the O was removed from the Rh by reduced ceria. This eliminated H₂O and CO₂ formation. The absence of these reaction channels, i.e. the reaction of C or H with O, resulted in H₂ and NH₃ formation at low temperatures. C_xN_y intermediates were now detected on the Rh at higher temperatures but these ultimately decomposed leading to N₂ and CO through the reaction of C with the ceria.

6.2.3 - Water and the Water-Gas Shift Reaction

Water was studied experimentally on Rh / CeO_x(111).[68] Water adsorbs weakly on oxidized CeO₂(111)[15,68] and on Rh(111) and polycrystalline Rh.[311] Therefore it isn't too surprising that water adsorption on Rh / CeO₂(111) showed little difference compared to water on CeO₂(111). Chen et al calculated that water adsorbed on Rh/CeO₂(111) was slightly more stable than water adsorbed on CeO₂(111).[312] This may be evident in a slight broadening of the H₂O desorption toward higher temperatures on Rh/CeO₂(111) but the effect is not substantial.[68] When H₂O was adsorbed on reduced Rh / CeO_{2-x}(111) there was a new H₂ desorption state between 250 K and 300 K and the high temperature H₂ desorption state near 600 K from H₂O on CeO_{2-x}(111) (see Figure 12) shifted to lower temperature. The Rh facilitated the disproportionation of –OH on the oxide surface to produce H₂. The persistence of two H₂ desorption features may be due to –OH located near the Rh/CeO_{2-x}(111) interface (the low temperature peak) and –OH located away from the interface that diffused to the Rh at higher temperature.

Much of the interest in water adsorption on M/CeO_x stems from research in the water-gas shift reaction (WGS).

Studies have determined that $\text{CeO}_2(111)$ without supported metal is inactive for WGS.[65,266,313] The WGS activity increases substantially for Cu[313], Au[313,314], Ni[266] and Pt[65] supported on ceria. The WGS activity is optimal at submonolayer coverages of the metals indicating that reaction likely occurs at the interface between the oxide support and metal nanoparticles.

Co-adsorption of CO and H_2O was studied on $\text{Rh/CeO}_x(111)$.[68] Any interaction between CO and H_2O was presumed to be bi-functional, i.e. water adsorbed on the ceria and CO adsorbed on the Rh, since CO does not adsorb on the ceria[171,279,315] and water doesn't adsorb on Rh above 300 K[311] in UHV. Since water also desorbs at low temperature from oxidized $\text{CeO}_2(111)$ the CO and H_2O were co-adsorbed on Rh / $\text{CeO}_{2-x}(111)$. No CO_2 was observed during thermal desorption indicating that WGS did not occur in the UHV co-adsorption experiment. However, co-adsorption of CO and H_2O affects the desorption of H_2 and CO compared to H_2O or CO adsorbed individually. Molecular CO adsorbed on the Rh inhibits H_2 desorption near 300 K suggesting that the CO blocks the reaction of $-\text{OH}$ at the ceria/Rh interface. CO on reduced $\text{Rh/CeO}_{2-x}(111)$ dissociates above 300 K. The co-adsorbed water does not inhibit the dissociation. However the recombination of $\text{C} + \text{O}$ to desorb as CO occurs at a slightly lower temperature when the ceria is covered by $-\text{OH}$. Since isotopic labeling experiments indicated that C is reacting with O on the ceria[76] the presence of $-\text{OH}$ enhances the reactivity between the C and the oxide.

The adsorption of water on various $\text{M/CeO}_2(111)$ surfaces has been studied computationally, particularly as it relates to the WGS reaction. In many of these studies a consistent observation was that the dissociation of water was the rate limiting step in the WGS reaction. On Cu_4 clusters on $\text{CeO}_2(111)$ Yang et al determined that Cu_4 becomes positively charged which promotes the dissociation of H_2O .[256] Liu and Rodriguez studied Cu_{29} and Au_{29} clusters.[316] Water dissociation was found to be more favorable at the edges and corners of the nanoparticles. It wasn't clear what synergistic effect the ceria surface played in the process. On a Rh_4 cluster on $\text{CeO}_2(111)$ Chen et al determined that both CO and H_2O adsorbed on the Rh.[312] Dissociation of the water led to the formation of a carboxyl intermediate (Rh-COOH) which then decomposed to CO_2 and H. Finally, Bruix et al [65] and Senanayake et al [317] reported a "new type of strong metal-support interaction" for Pt and Ni nanoparticles on $\text{CeO}_2(111)$. DFT calculations and valence photoemission indicated a smaller density of Pt 5d or Ni 3d states near the Fermi level compared to bulk metallic Pt or Ni. These nanoparticles enhanced the ability to adsorb and dissociate water relative to the bulk metals. This unique

property of small metallic clusters was consistent with experimental observations that sub-monolayer amounts of Pt, Au, Cu and Ni promoted the WGS reaction.

6.2.4 – Alcohols and Formic Acid

The adsorption of methanol on Rh/CeO_x(111)[318] produces desorption features that are different from methanol on either CeO_x(111)[83,205,208], Rh(111)[319] or Rh(100).[320] Methanol dissociates and adsorbs as H and methoxy on both the ceria surface and Rh particles. The TPD spectra in Figure 31 can be interpreted in terms of methoxy decomposing on the Rh particles and methoxy adsorbing on the ceria and then reacting at the Rh/CeO_x(111) interface. The H₂ desorption below 300 K and the CO desorption near 500 K are consistent with what has been observed following methanol adsorption on Rh(111)[319] and Rh(100).[320] Methanol adsorbed on Rh-free ceria disproportionates to formaldehyde and methanol near 600 K (Figure 20). When Rh is present the formaldehyde formation is completely suppressed and only CO and H₂ are produced. The CO and H₂ associated with the methoxy adsorbed on the ceria are produced at a lower temperature than where formaldehyde and methanol are produced on clean ceria. These results indicate that the methoxy on the ceria is reacting at the Rh / ceria interface. The reaction kinetics do not depend on the amount of Rh present nor the size of the Rh particles. A single, sharp CO desorption peak, coincident with a sharp H₂ peak, indicates that all of the methoxy on the ceria is reacting at the Rh / ceria interface. TPD and C 1s sXPS indicate that at low methanol exposures all of the methanol adsorbs and reacts on the Rh nanoparticles. This is evidence of the so-called “capture zone” effect[321,322] where methanol that has impinged on the ceria rapidly diffuses to the Rh nanoparticles where it is bound more strongly and “captured” by the Rh. When methanol is adsorbed on reduced Rh/CeO_{2-x}(111) the CO that is produced through decomposition of methoxy on the Rh can undergo further decomposition to C + O just as CO does directly on Rh / CeO_{2-x}(111). [76,279]

Methanol was also studied on Pt / CeO₂(111).[323] The principal observation was that the methanol decomposed in a manner similar to methanol on sputtered, i.e. roughened, Pt(111). Specifically the methoxy was bound more strongly than on flat Pt(111) and that a portion of the C-O bonds were activated producing C on the Pt. The similarity of the behavior on sputtered Pt(111) and Pt / CeO₂(111) suggests that the morphology of the nanoparticles dictates the reactivity of methanol on the Pt.

Formic acid was studied on Pt / CeO₂(111).[62] TPD spectra from formic acid on CeO₂(111) without and with Pt are shown in Figure 22a and 22d, respectively. The presence of Pt increased the production of CO₂, CO, H₂ and H₂O. The results were attributed to spillover

from Pt to the ceria. The H₂ desorption results from reverse spillover from ceria to the Pt as was observed for both water and methanol on Rh/CeO_x(111). In addition, methane was produced from HCOOH / Pt / CeO₂(111) which was not observed in the absence of Pt.

Ethanol has been studied experimentally on Co / CeO₂ / YSZ(100)[324] and computationally on Rh / CeO_x(111).[325,326] Martano and Vohs observed that Co supported on reducible CeO₂ was more effective in the partial oxidation of ethanol to acetaldehyde compared to Co on non-reducible YSZ(100).[324] They attributed this behavior to the partial oxidation of Co⁰ to Co²⁺ by the ceria support. Ho et al have calculated the adsorption and decomposition of ethanol on Rh₁ / CeO₂(111)[325] and Rh₄ clusters on CeO₂(111)[326]. They determined that the ethanol adsorbs preferentially at a Ce cation site as opposed to an O anion or the Rh metal. The ethoxy then forms a metallocycle, Ce-O-CH₂-CH₂-Rh. From this configuration it undergoes dehydrogenation, C-C bond scission and oxidation by surface O to produce CO₂, CO, H₂O and H₂.

6.2.5 – SO₂

SO₂ adsorption and decomposition has been investigated on Cu,[327] Au,[327,328] and Pt[63] on CeO₂(111). The behavior in these three systems contrasts with SO₂ on metal-free CeO₂(111)[191,193,196] and on Cu[329,330], Au[331] and Pt[332-335] single crystal surfaces. SO₂ reacts with the O anions on CeO₂(111) to form SO₃²⁻[191,196] or SO₄²⁻[193]. These species desorb at higher temperatures as SO₂ without decomposition to S⁰ or S²⁻ on the surface. SO₂ adsorbs weakly as SO₂ on Au(111) and leaves the surface upon annealing to 150 K. [331] SO₂ adsorbs molecularly in two different configurations, standing up and lying down, on Pt(111).[332,333] Streber et al concluded that the SO₂ desorbed molecularly with little decomposition.[332] More highly stepped Pt surfaces led to the formation of SO₃²⁻ and S⁰. [335]. SO₂ interacted more strongly with Cu(111), Cu(100)[329] and Cu(110)[330] with some of the SO₂ decomposing to S⁰.

When the metals are supported on CeO₂(111) the interaction with SO₂ strengthens. SO₂ still doesn't decompose on Au / CeO₂(111) but the SO₂ persists to above 250 K. [327,328] On Cu / CeO₂(111) the decomposition to S⁰ is enhanced compared to Cu single crystals. The activity peaks at Cu coverages between 0.5 and 1.0 ML and decays back toward the activity of Cu metal at higher coverages.[327] The behavior of SO₂ on Pt / CeO₂(111) is perhaps the most complex.[63] Upon adsorption at 150 K the SO₂ adsorbs as sulfite, SO₃²⁻, on the CeO₂(111) and as SO₂ standing upright on the Pt nanoparticles based on the S 2p sXPS photoemission spectra. This is consistent with what was observed on metal-free CeO₂(111)[191] and on

Pt(111)[332,333] except for the absence of lying down SO_2 on the Pt nanoparticles. As the sample is heated SO_3^{2-} and SO_2 disappear and S^0 is formed. At the highest temperatures the S^0 is transformed into oxysulfide species on the ceria. These transformations are accompanied by changes in the Ce oxidation state. As the sample is heated from 150 K to 300 K the Ce^{3+} population increases. Upon further heating the Ce^{3+} population decreases. Hapel et al interpreted these results to indicate that negatively charged $\text{SO}_x^{\delta-}$ species migrated from the ceria onto the Pt nanoparticles. This led to an increase in Ce^{3+} and a loss of SO_3^{2-} on the ceria. The $\text{SO}_x^{\delta-}$ then decomposed on the Pt into S^0 and the O returned to the ceria resulting in the oxidation of Ce^{3+} to Ce^{4+} . At the highest temperatures the S spilled off of the Pt and reacted with the ceria to create the oxysulfide.

6.2.6 – Hydrocarbons

As noted in Section 5.2 non-functionalized hydrocarbons have not been extensively studied on clean cerium oxide surfaces. It appears that ethylene does not adsorb strongly nor react on $\text{CeO}_2(111)[201]$ nor on $\text{CeO}_2 / \text{YSZ}(100)[202]$ When Rh or Pt are supported on the ceria surfaces the ethylene adsorbs on the metal particles and decomposes. On Rh single crystal surfaces ethylene thermally decomposes to produce gaseous H_2 leaving C on the surface.[336-338] The H_2 desorbs from the Rh between 300 K and 500 K. If Rh is supported on an inert substrate such as $\alpha\text{-Al}_2\text{O}_3(0001)$ the ethylene decomposes in a similar manner and H_2 desorbs near 440 K.[170] When ethylene is adsorbed on Rh / $\text{CeO}_2(111)[201]$ or Rh / $\text{CeO}_2 / \alpha\text{-Al}_2\text{O}_3(0001)[170]$ CO is produced in addition to H_2 . The CO results from a reaction between C on the Rh particle and O on the ceria substrate. During successive cycles of ethylene adsorption followed by TPD the CO desorption temperature moves to progressively higher temperatures indicating that it becomes more difficult to remove O from an increasingly reduced surface.[170] On Rh / $\text{CeO}_2 / \text{YSZ}(100)$ ethylene decomposition produces CO_2 in addition to CO and H_2 . [202] This demonstrates that the YSZ(100) substrate alters the reactivity of the O in the CeO_2 . Notably H_2O is not observed in any of these Rh / CeO_2 systems indicating that the H atoms combine and desorb as H_2 rather than react with O in the ceria.

Similar behavior is observed for ethylene adsorbed on Pt / $\text{CeO}_2(111)$. [339] The TPD was not reported but the C 1s sXPS indicated decomposition of the ethylene to C on the Pt followed by removal of the C at high temperature. The removal of the C coincided with an increase in the Ce^{3+} content indicating reduction of the ceria through the reaction of O with the C. Compared to Pt(111) the Pt nanoparticles on $\text{CeO}_2(111)$ activated the dehydrogenation of the ethylene at a lower temperature. Enhanced dehydrogenation activity was also observed for

methane on Pt / CeO₂(111).[340,341] At temperatures near 100 K methane partially dehydrogenates to CH₃ which is then stable on Pt(111). On Pt nanoparticles on CeO₂(111) the methane further dehydrogenates to CH. H spillover was observed through the formation of OH on the ceria. Enhanced methane activation was also observed for model low-surface area Pd, Pt and Rh on CeO₂ during methane steam reforming.[342]

6.3 – Inverse Catalysts

In a typical, conventional catalyst a metal is supported on an oxide substrate. In an inverse catalyst oxide nanoparticles are supported on a bulk metallic substrate (Figure 32).[343] The utility of an inverse catalyst may seem counterintuitive since a conventional catalyst is partly designed to maximize the surface area of the more active, and frequently more expensive, metallic component. However, as discussed by Rodriguez and Hrbek in their perspective article on inverse catalysts, these structures provide fundamental insight into the nature of the metal/oxide interface because the properties of oxide nanoparticles may be influenced by defects, edge and corner sites, strain, and electronic interactions with the metal which are absent on ideal, flat oxide surfaces.[343] Such studies therefore further close the gap between model systems and real catalysts. Reactions have been studied on ceria nanoparticles supported on Au(111)[86,164,344], Rh(111)[345], Pt(111)[84,85,346,347] and Cu(111).[87,107,347-350]. In this section we will not focus on the structural characterization of these systems but rather discuss their reactivities and how they may differ from the conventional metal on ceria behavior.

Studies on inverse ceria on metal model catalysts have primarily focused on the CO oxidation reaction, $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$, and the water-gas shift reaction (WGS), $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$. These model catalysts have been studied both under reaction conditions as well as the adsorption properties of some of the individual components such as CO, O₂ and H₂O. One of the earliest studies examined the adsorption of CO on O-covered Rh(111) with and without ceria nanoparticles[345]. Eck et al observed that the adsorption of CO at 300 K proceeded more slowly on O/Rh(111) compared to clean Rh(111). They attributed this to the rate limiting kinetics of the CO + O oxidation reaction that inhibited CO uptake on the surface. However, when ceria was present on the Rh surface the CO + O reaction was much faster. They attributed this to unique CO adsorption sites at the metal-ceria interface.

Weiss et al have studied CO adsorption and CO oxidation on the ceria / Pt(111) inverse catalyst. They observed that the Pt promoted the reduction of CeO₂ via spillover of CO from the Pt surface to the ceria.[347] They also studied the oxidation of CO on Pt(111) and ceria /

Pt(111) as a function of the CO partial pressure relative to O₂. [84,85] As shown in Figure 33 the oxidation reaction shows a high-rate region and a low-rate region as the CO pressure is increased and also exhibits hysteresis when the CO pressure is reduced. This behavior is attributed to a poisoning effect of CO on the Pt which inhibits adsorption and dissociation of O₂ on the surface. The presence of ceria on the surface has two effects. First the overall rate of reaction is enhanced despite the fact that the ceria blocks some of the adsorption sites on the Pt. In addition, the pressure at which the reaction shifts from high-rate to low-rate, τ_A , shifts to higher pressure when ceria is present. They attributed the enhanced activity to an increased O₂ dissociation rate at the ceria / Pt interface. The shift in the transition pressure, τ_A , was attributed to O spillover from the ceria to the Pt which supplied O for the reaction after CO blocked the sites on the Pt surface.

Rodriguez et al have produced a number of studies involving inverse ceria catalysts on Cu(111) and Au(111). As a general observation they reported that the CO oxidation reaction[87,351] and the WGS reaction[86,351-353] was enhanced on the inverse catalysts. In both of the reactions the unique contribution of the ceria is to adsorb and dissociate either O₂ or H₂O. This part of the reaction pathway is either slow or essentially non-existent on the clean Cu or Au surfaces. They observed that when water was adsorbed on ceria / Au(111) the water dissociated on partially reduced CeO_{2-x} and that the water was unable to fully oxidize the ceria particles which maintained their water dissociation activity.[344] Using synchrotron-based sXPS they studied the WGS reaction intermediates in UHV on ceria / Au(111)[164] and 90 mTorr CO / 30 mTorr H₂O on ceria / Cu(111).[81] On ceria / Au(111) they determined that when the ceria was highly oxidized there was an absence of OH on the ceria and the primary surface species was carbonate (CO₃)²⁻, but when the ceria was reduced the presence of OH resulted in formate intermediates (HCOO-) on the surface. At elevated pressure under reaction conditions on ceria / Cu(111) they determined that the reactive intermediate was CO₂^{δ-}.

7 – Summary and Outlook

Adsorption and reaction on cerium oxide surfaces are clearly related to the key concepts highlighted in the **Introduction**: 1) the coordination environment of the surface atoms; (2) the redox properties of the oxide; and (3) the oxidation state of the surface.[6] It was established in the earliest work on CeO_x(111) that reduced CeO_{2-x}(111) is much more chemically active than oxidized CeO₂(111). However, the reduction of CeO₂(111) alters all three of these important oxide characteristics. The removal of an O anion from the surface creates an additional coordination vacancy on the neighboring Ce cations, it becomes more difficult to remove

subsequent O from the surface, and two Ce cations change from Ce^{4+} to Ce^{3+} . We can postulate certain outcomes based on these changes which appear to be consistent with experimental observations. The change in the Ce coordination produces a more stable adsorption site for many reactants. However, the decrease in reducibility results in products containing less O; in some cases resulting in unreacted elements such as S or C remaining on the surface.

The vast majority of experimental studies have been conducted on the (111) surface. However, it is clear from recent observations that the (100) surface behaves very differently. This is again to be expected since, as shown on the reconstructed surface in Figure 7b, both the Ce and the O have two coordination vacancies compared to only one coordination vacancy for the Ce and O on $\text{CeO}_2(111)$ (Figure 6). The result is that for adsorbates such as water, CO_2 and organic oxygenates, $\text{CeO}_2(100)$ is more reactive in the sense that these reactants form much more stable surface species on $\text{CeO}_2(100)$ compared to $\text{CeO}_2(111)$. Further, it has been determined computationally that $\text{CeO}_2(100)$ has a lower O-vacancy formation energy than $\text{CeO}_2(111)$.^[7-9] The observable result is a greater prevalence of O-containing reaction products from $\text{CeO}_2(100)$. The more under-coordinated O on $\text{CeO}_2(100)$ appears to make this surface more nucleophilic. Organic oxygenates adsorbed on $\text{CeO}_2(100)$ are susceptible to a loss of H resulting in CO, CO_2 and water as reaction products.

To date there have been no experimental studies of adsorption and reaction on $\text{CeO}_2(110)$. This surface may produce reaction properties that are an interesting hybrid between those observed on $\text{CeO}_2(111)$ and $\text{CeO}_2(100)$. The Ce on the $\text{CeO}_2(110)$ surface (Figure 5) has two coordination vacancies as does the Ce on $\text{CeO}_2(100)$ (Figure 7b). This suggests that many adsorbates will readily adsorb on the $\text{CeO}_2(110)$ surface. However, the O only has one coordination vacancy, perhaps resulting in a less nucleophilic surface and more selective reaction products. This hypothesis needs to be tested.

There have been numerous computational studies on cerium oxide surfaces. This has enabled a direct comparison of theory and experiment. Ideally, as the computational tools become more wide spread they will enable guidance for experimental directions of investigation. While there have been many calculations on the $\text{CeO}_2(111)$ surface there has been somewhat of a mismatch between theory and experiment regarding $\text{CeO}_2(100)$ and $\text{CeO}_2(110)$. There have been many calculations, but no experiments, on $\text{CeO}_2(110)$, and, conversely, more experiments but fewer calculations on $\text{CeO}_2(100)$. From the experimental end the lack of studies on $\text{CeO}_2(110)$ presumably has been the result of the difficulty in preparing a suitable surface. $\text{CeO}_2(100)$ is more difficult from a computational perspective as it is unclear what surface model

to utilize to overcome the polarized surface problem. Advances from both the experimental and computational direction will presumably close this gap.

Reactions on metals supported on ceria surfaces have been somewhat limited and there have been essentially no studies on metals supported on $\text{CeO}_2(100)$ and $\text{CeO}_2(110)$. Early studies examined primarily NO, CO and simple hydrocarbons. Presumably these experiments were motivated by the application of ceria in automotive exhaust catalysts. More recent investigations have focused on the outstanding activity of ceria as a component in water-gas shift catalysts. Other, more complex, reactants would appear to be a fertile area for exploration on metal / ceria surfaces.

It also appears that many of the metal / ceria combinations operate as bi-functional catalysts, i.e. one reactant adsorbs on the metal while another adsorbs on the oxide. Utilizing ceria surfaces other than $\text{CeO}_2(111)$ will presumably alter the activity as reactants will interact differently with the other ceria surfaces.

Finally, it is now possible to create high surface area cerium oxide nanocrystals that expose primarily specific, low-index crystallographic faces.[354-357] As shown in Figure 34, it is possible to synthesize cubes that expose $\text{CeO}_2(100)$ facets (Figure 34c and 34d), and octahedra that expose $\text{CeO}_2(111)$ facets (Figure 34e and 34f).[157] These nanoshapes are not ideal, however, and each shape exposes defects at edges and corners as well as an undetermined number of vacancies on their faces. These defects presumably become more pronounced as the sizes of the particles get smaller. Such complexities will need to be addressed by systematically incorporating defects into the well-defined experimental surfaces and computational models. These experiments will help elucidate the role of defects in the behavior of ceria-based “real world” catalysts.

8 - Acknowledgments

I wish to thank Peter Albrecht for his invaluable assistance in conducting the literature review for this report. This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division.

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Figure Captions

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Atomic-scale resolution STM image of a 3-nm-thick reduced $\text{CeO}_{1.75}(111)$ on $\text{Ru}(0001)$. Images were taken with a constant current STM mode (3-4 V and 0.5-1.0 nA). Reprinted with permission from Ref.[34]. Copyright 2008 American Chemical Society.

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Conventional Catalyst

Inverse Catalyst

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