

The surface chemistry of cerium oxide<sup>☆</sup>

David R. Mullins\*

Chemical Sciences Division, Oak Ridge National Laboratory, PO Box 2008, MS 6201, Oak Ridge, TN 37831-6201, USA

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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<sub>2</sub> to CeO<sub>2–x</sub>. 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.

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**Keywords:** Ceria; Thin films; Scanning tunneling microscopy; Temperature programmed desorption; Photoelectron spectroscopy; Chemisorption**Contents**

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**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

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\*Tel.: +1 865 574 2796; fax: +1 865 241 5252.

E-mail address: [mullinsdr@ornl.gov](mailto:mullinsdr@ornl.gov)

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## 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 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 H<sub>2</sub> (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 Ce<sup>4+</sup> to Ce<sup>3+</sup>. 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 CeO<sub>2</sub> 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

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