Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Investigation of trimethylacetic acid adsorption on stoichiometric and oxygen-deficient $CeO_2(111)$ surfaces

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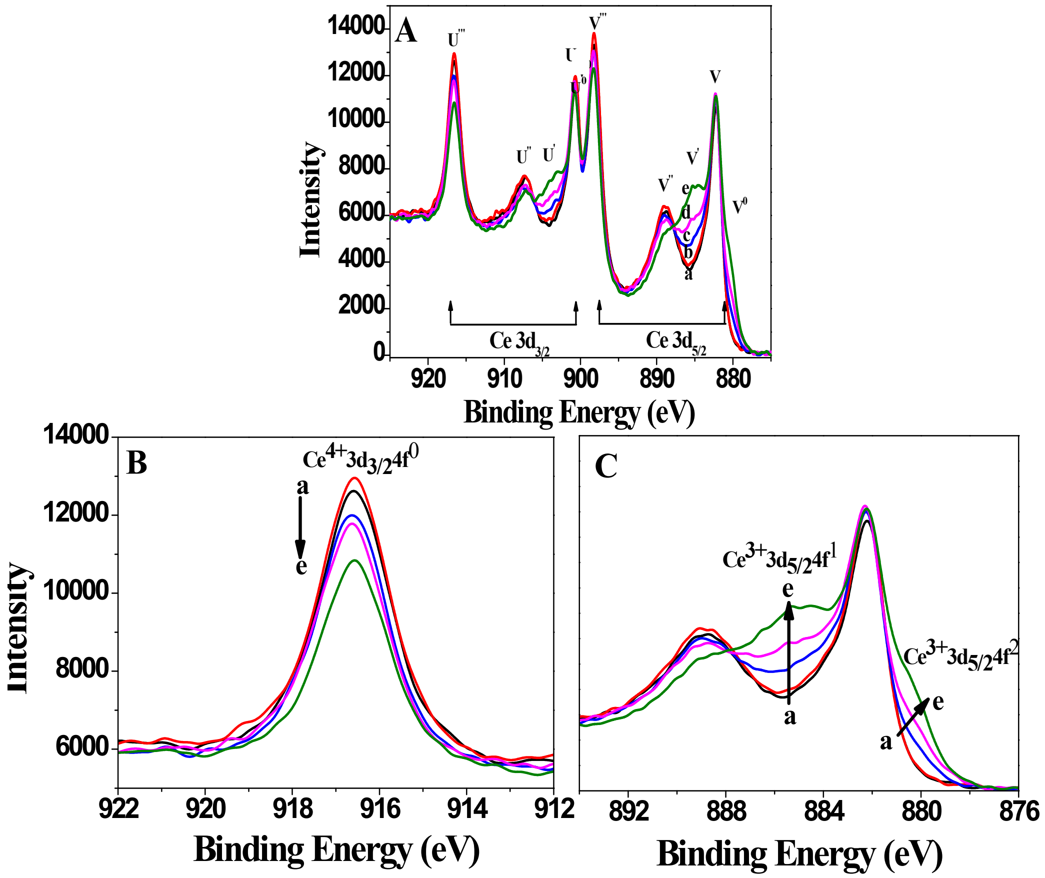
SI-1 Vacuum annealing of cerium oxide to create oxygen deficient ceria surface



SI-1: The Ce 3d x-ray photoelectron spectra (XPS) characteristic of both Ce^{3+} and Ce^{4+} measured from $CeO_2(111)$ film on YSZ(111) following (a) annealing at ~550°C in ~2.0x10^{-5} Torr of O_2 for 30min as well as sequential annealing in ~1.0x10^{-9} Torr of vacuum at (b) ~550°C, (c) ~650°C, (d) ~750°C and (e) ~850°C for 30min each (A). The panels B and C show XPS bands characteristic of Ce^{4+} reduction to Ce^{3+} and growth of Ce^{3+}, respectively, with increasing annealing temperature from 550°C to 850°C in ~1.0x10^{-9} Torr of vacuum.

Description: The Ce 3d spectra consist of two sets of peaks corresponding to the spin-orbit splitting components, the bands labeled $v^{(n)}$ and $u^{(n)}$ correspond to the features from Ce $3d_{5/2}$ and Ce $3d_{3/2}$ core levels, respectively. Each of the Ce $3d_{5/2}$ and Ce $3d_{3/2}$ sets of peaks is composed of three features from CeO_2 (Ce^{4+}) and additional two features from Ce_2O_3 (Ce^{3+}) in the cases of partially reduced surfaces. The v, v´´ and v´´´ peaks can be attributed to CeO_2 where v and v´´ are due to a mixture of $(5d6s)^0$ $4f^2$ O $2p^4$ and $(5d6s)^0$ $4f^1$ O $2p^5$ configurations while v´´´ is a pure $(5d6s)^0$ $4f^0$ O $2p^6$ final state (Burroughs et al JACS-Dalton Transactions (1976), page 1686; Romeo et al Surface and Interfacial Analysis (1993), page 508) . In the case of Ce_2O_3; v^0 and v´

peaks are due to a mixture of $(5d6s)^0$ $4f^2$ O $2p^4$ and $(5d6s)^0$ $4f^1$ O $2p^5$ configurations. In the similar way the $u^{(n)}$ peaks can be attributed to Ce $3d_{3/2}$ features. The panels B and C of SI-1 show the detailed view of the Ce $3d_{3/2}$ $4f^0$, and Ce $3d_{5/2}$ $4f^1$ and $4f^2$ features respectively. A progressive reduction of CeO_2 into Ce_2O_3 will result in the decrease of the $4f^0$ features (v′′′ and u′′′) and an increase in the v^0, v′, u^0, and u′ (Romeo et al Surface and Interfacial Analysis (1993), page 508). Increase in the intensity of bands from Ce^{3+} $3d_{5/2}$ $4f^2$ at 880 eV (v^0), Ce^{3+} $3d_{5/2}$ $4f^1$ at 885 eV (v′), , Ce^{3+} $3d_{3/2}$ $4f^2$ at 900 eV (u^0), and Ce^{3+} $3d_{3/2}$ $4f^1$ at 905 eV (u′) indicates the surface reduction of Ce^{4+} cations to Ce^{3+} following the creation of oxygen vacancies with increasing annealing temperatures as shown in the enlarged v^0 and v′ peaks in panel C of SI-1. As the annealing temperatures increase, oxygen ions in ceria become more mobile and energetic, and leave the surface. Thus, oxygen deficient $CeO_{(2-\delta)}$ surface is accompanied by the presence of oxygen vacancies and extra electrons according to eqn. (1)

$$O^X \rightarrow V^{**} + 2e' + {}^1/_2O_2(g) \qquad (1)$$

where, O^X is an O^{2-} anion, V^{**} is an anion vacancy and e′ is an electron that localizes on the 4f orbital of Ce^{4+} cations (Skorodumova et al, PRL (2002) article 166601), effectively reducing it to Ce^{3+} (Creaser et al Catalysis Letters (1994), page 13). Thus, an increase in peak intensity of bands is observed on the lower binding energy side of the main bands with increase in vacuum annealing temperatures. Additionally, the Ce $3d_{3/2}$ $4f^0$ band (u′′′) at 916.7 eV shown in panel B of SI-1 is solely attributed to the Ce^{4+} state of CeO_2 and is attenuated as the sample surface is progressively annealed in vacuum at higher temperatures.

To quantify the reduction of surface cerium ions deconvolution of the Ce 3d XPS spectra becomes difficult because of the overlapping of photoemission lines from different spin orbitals of Ce^{4+} and Ce^{3+} (Henderson et al Surface Science (2003), page 1). Previous studies (Henderson et al Surface Science (2003), page 1; Hoang et al Applied Surface Science (1993), Page 55; Mullins et al Surface Science (1999), Page 186)have reported a linear correlation between the attenuation of Ce $3d_{3/2}$ $4f^0$ band with the extent of surface reduction and have used this attenuation factor to resolve the amount of surface reduction as compared to a clean stoichiometric surface. Using an identical approach we performed a Gaussian-Lorentzian type curve fitting with a Shirley background for the ten bands in the Ce 3d spectra to quantify the area under each band. The area under the bands associated with the Ce^{3+} species increases as the sample is annealed at higher temperatures in contrast to the decrease in the area of the peaks associated with Ce^{4+} species. After normalizing the area under the 916.7 eV band with cerium concentration in each sample, the concentration of Ce^{3+} was found to be 7.5%, 17% and 25% for samples annealed in vacuum at 650°C, 750°C and 850°C respectively. No major change was observed in samples annealed in vacuum at 550°C. Thus increasing the vacuum annealing temperatures creates oxygen vacancies on CeO_2 (111) surface according to equation 1 and the extra electrons from oxygen localizes on cerium ions increasing the concentration of Ce^{3+} ions. Thus vacuum annealed surface consists of a mixture of Ce^{3+} and Ce^{4+} cations along with oxygen vacancies that is similar to the features observed on CeO_2 nanoparticles surface.

SI-2: Estimation of surface coverage

The surface coverage of TMAA on CeO_2(111) films was calculated by using the electron attenuation length (EAL) approach by Henderson *et.al.* (Surface Science (2003), page 1) from a model developed by Powell and Jablonski (Surface Science (2002), page 78) at the National Institute of Standards and Technology. Powell et al estimated that 27% of the total Ce $3d_{3/2}$ $4f^0$ signal is detected from the first layer and 90% of the signal came from layers 1 through 7. These simulations were performed using the molecular weight, density, number of valence band electrons and band gap for ceria. A monolayer corresponds to 3.1Å thickness of CeO_2(111) thin film. Based on these estimations and our elemental composition it was calculated that 8.235% and 7.965% atomic cerium was probed on the surfaces of TMAA adsorbed on stoichiometric and oxygen deficient CeO_2(111), respectively. The XPS elemental quantification yields 8.9 % and 12.3% total carbon on the stoichiometric and oxygen deficient CeO_2 (111) surface following TMAA adsorption. Since, all of the probed carbon originates from the chemisorbed TMAA molecules and each TMAA molecule contains 5 carbon atoms, therefore 1.78 % (8.9%/5) and 2.46 % (12.3%/5) TMAA molecules are present on the surface. The surface coverage is defined as the total numbers of available cerium sites covered by TMAA molecules i.e. the ratio of the number of TMAA molecules to the number of cerium sites available on the surface of the film. From the quantification numbers calculated above the surface coverage of TMAA molecules adsorbed on stoichiometric and oxygen deficient CeO_2 (111) surfaces is found to be 0.22ML and 0.30ML respectively.