Gas-Solid Interaction of H_2-$Ce_{0.95}Zr_{0.05}O_2$: New Insights on Surface Participation in Heterogeneous Catalysis

Ruchi Jain,[1] Anjani Dubey,[1] Manoj K Ghosalya[1] and Chinnakonda S. Gopinath[*,1,2]*

Electronic Supplementary Information

SI-1: Characterisation:

X-Ray diffraction analysis. The X-ray diffraction pattern and Raman spectrum of $Ce_{0.95}Zr_{0.05}O2$ (CZ) thin film is shown in Fig.S1a and Fig. S1b, respectively. Diffraction pattern shown in Fig. S1a confirms the cubic fluorite structure of CZ thin film with preferentially oriented facets of (111), (200), (220) and (311). Sharp and high intensity diffraction peaks observed at 47.8 º and 56.4 º is from the silicon substrate and it is indexed to (220) and (311) peak of silicon. Since no peak appeared for zirconia so we can clearly indicates the formation of ceria zirconia solid solution. The broad peak shows that film formed is nanocrystalline in nature with a crystallite size of 6 nm as calculated from Scherrer formula.

Raman Analysis: Raman spectra of $Ce_{0.95}Zr_{0.05}O_2$ thin film has been shown in Fig. S1b. Peak around 461.6 cm^{-1} is the characteristic peak for CZ film which corresponds to Raman active mode vibrational feature of Ce-O bond. The broadening of Raman line for Ceria corresponds to smaller crystallite size. The peak at 304.1, 521.1, 620.4 and 667.2 cm^{-1} is from the silicon substrate. There is no peak for ZrO_2 was observed in Raman spectrum, which clearly indicates that Zr^{4+} ion sits in lattice of ceria. No significant difference in Raman spectrum was observed after reduction.

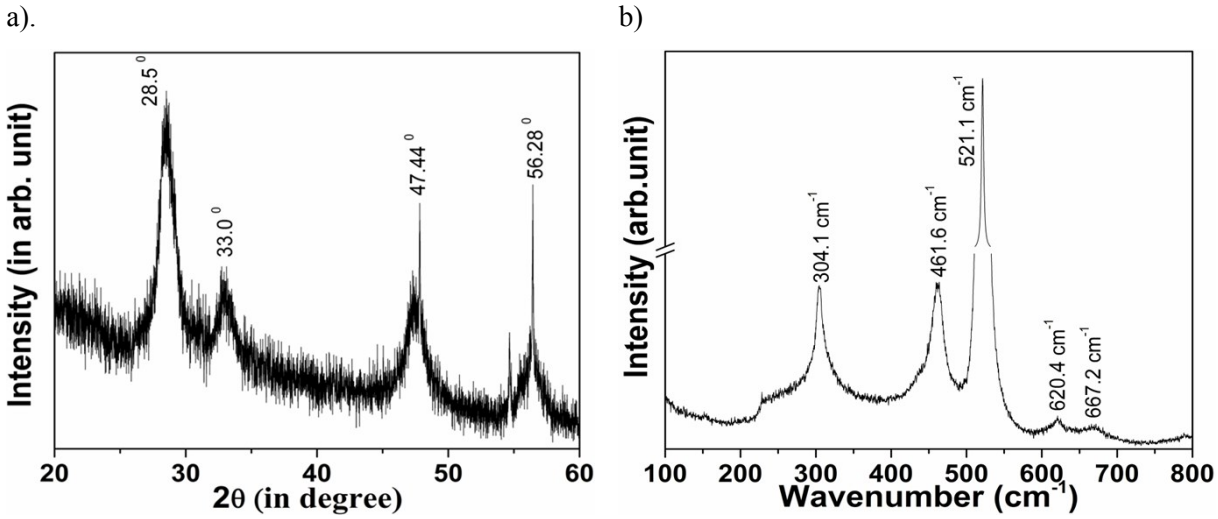

Figure S1. ***(a)*** XRD pattern of $Ce_{0.95}Zr_{0.05}O_2$ thin film with cubic fluorite structure. (b) Raman spectra for $Ce_{0.95}Zr_{0.05}O_2$ thin film.

SI-2: XPS of Zr 3d core level : Temperature dependent study

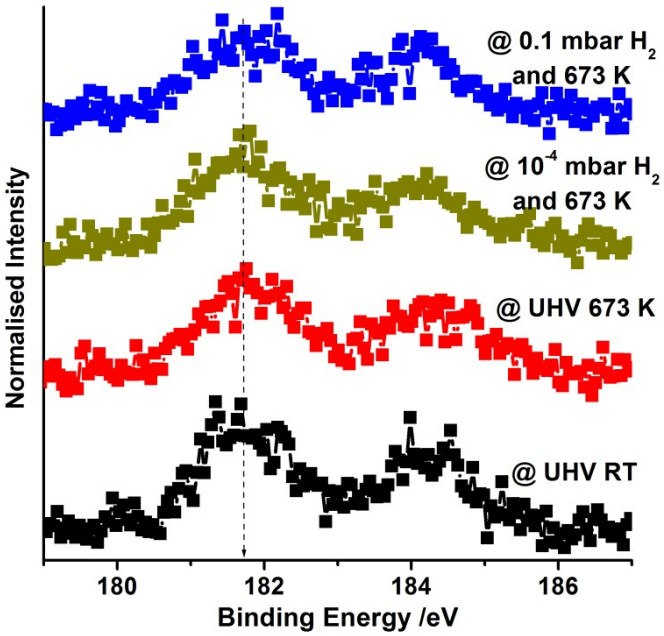

Figure S2: A systematic change in the core level spectra of Zr 3d at different experimental conditions.

SI-3: XPS of sputtered CZ surface

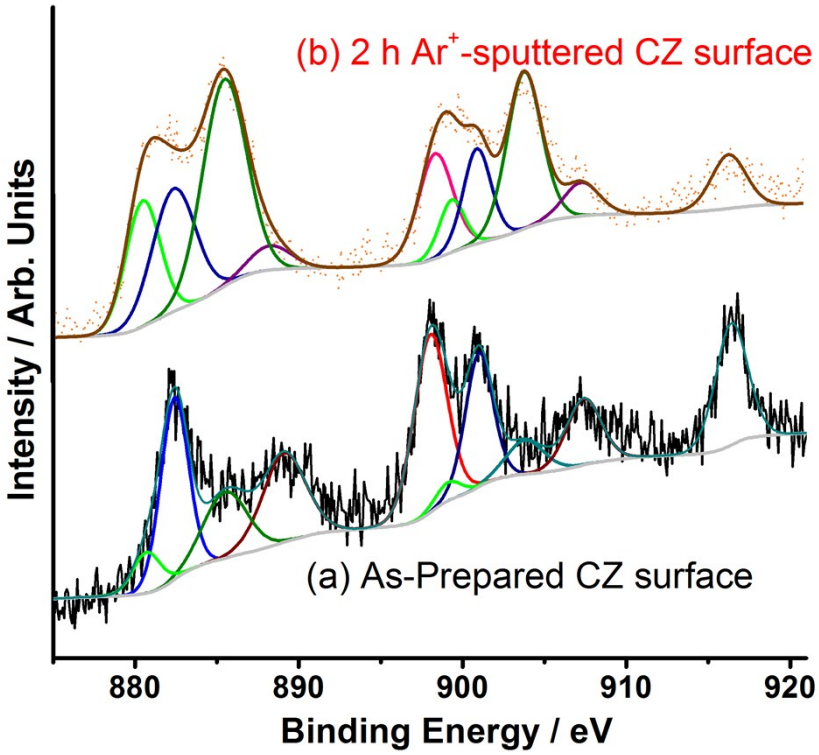

Figure S3: Ce 3d core level XPS was recorded for as prepared and 2 h Ar^{+}-sputtered CZ surfaces and the results are compared. A great increase in Ce^{3+} features are observed highlights the removal of surface oxygen atoms.

SI-4: Pressure dependent study:

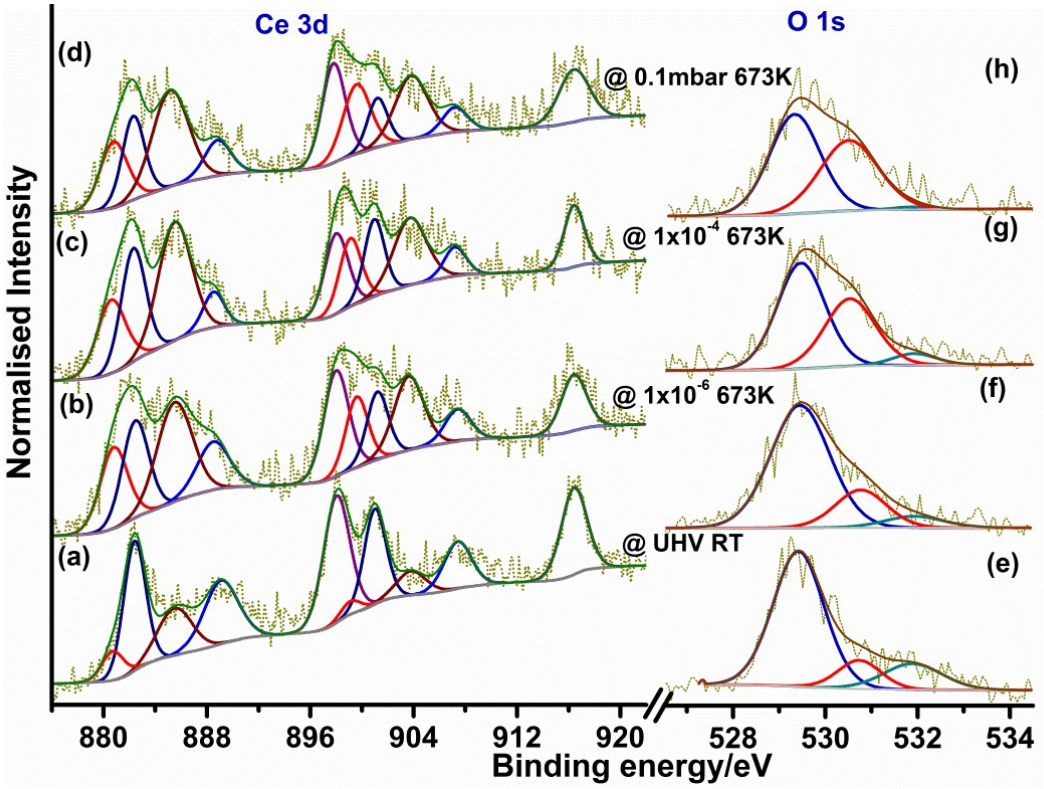

Figure S4: A systematic change in the core level spectra of Ce 3d and O 1s at different conditions. (a and e) spectra at UHV RT, (b and f) UHV at 673 K, (c and g) 10^{-4} mbar H_2 at 673 K , and (d and h) 0.1 mbar H_2 at 673 K.