Supporting Information

Defect Site Promoted Surface Re-organization in Nanocrystalline Ceria for the Low Temperature Activation of Ethylbenzene

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Synthesis of Ceria samples:

Ceria-A sample was prepared by the dissolution of $Ce(NO_3)_3.6H_2O$ in an aqueous ethanolic solution followed by slow precipitation using dilute NH_3 (2%) at pH 7. The hydroxide gel formed was stirred at 353 K for 3 h, as the solvent evaporated. The solid obtained was dried at 393 K for 12 h and calcined at 723 K for 4 h. The other ceria samples (ceria-P, ceria-U and ceria-G) were prepared as per procedure given in Ref. 4.

Electron Paramagnetic Resonance Spectroscopy:

EPR measurements were conducted on a Bruker EMX X-band spectrometer ($\upsilon \approx 9.4$ GHz) operating at a 100 kHz field modulation. The ceria sample (~ 80 mg) was taken in a specially designed quartz EPR cell (o.d.= 4 mm) fitted with greaseless stopcocks and having a provision for adsorption and desorption of gases.

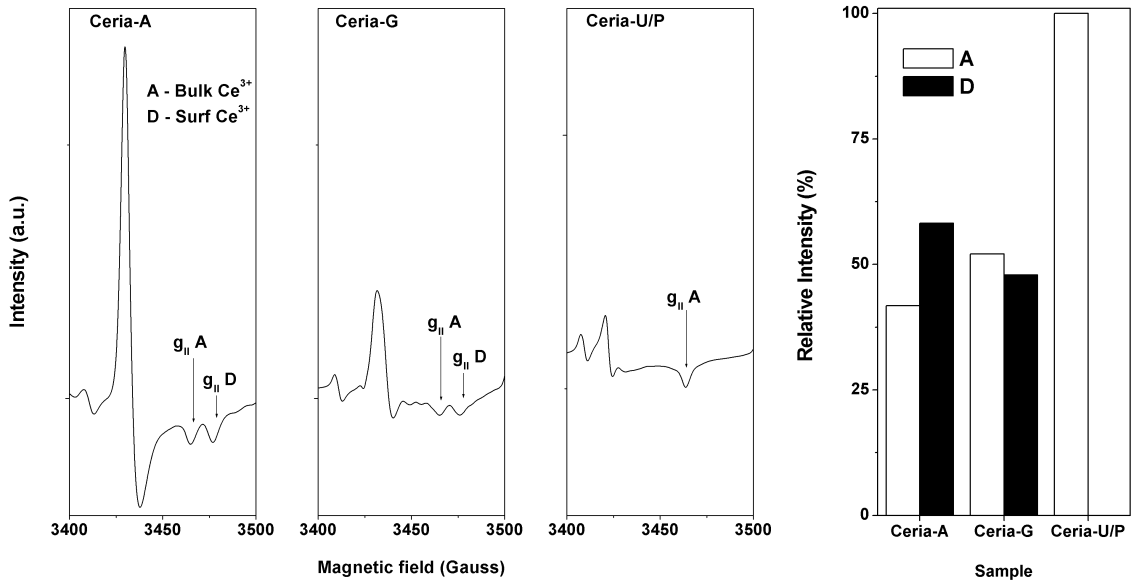


Figure S1. Electron paramagnetic resonance spectra of ceria samples prepared by various routes. The spectra are recorded at 298 K under atmospheric pressure. The relative intensity in percentage of the $g_{||}$ signals corresponding to A (Ce^{3+} ions in the bulk of the solid, stabilized by some lattice defects) and D (Ce^{3+} ions with easily removable ligands, prominently on the surface) is also presented. The surface to bulk defect ratio follows the order Ceria-A > Ceria-G > Ceria-U/P.

Temperature programmed reduction:

Temperature-programmed reduction (TPR) experiments were performed on a Micromeritics Autochem 2910 instrument. A weighed amount of the sample (~125 mg) was placed in a quartz reactor, pretreated in a flow of Ar (99%) at 773 K for 1 h and cooled to 298 K. A gas mixture of H_2 (5%)-Ar (95%) was then allowed to flow (25 ml min^{-1}) through the reactor. The temperature was raised to 973 K at a heating rate of 10 $K.min^{-1}$. A thermal conductivity detector (TCD) attached at the outlet of the reactor provided a measure of the volume of hydrogen consumed during the reduction experiments.

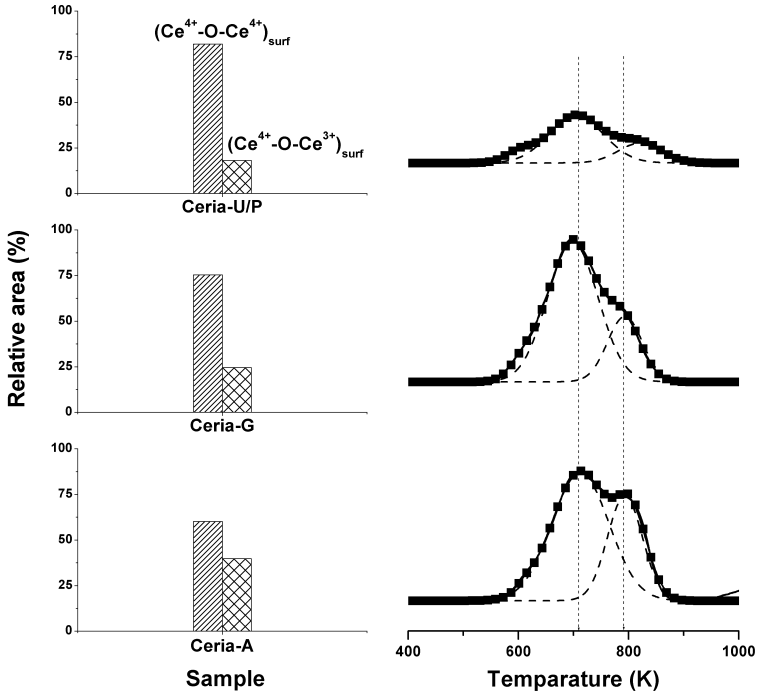
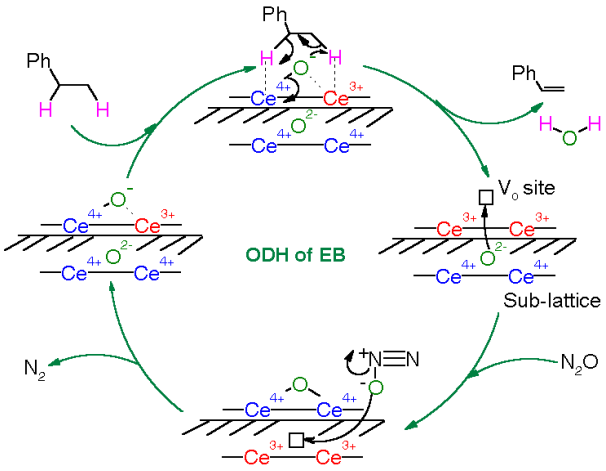


Figure S2. Temperature programmed reduction profile of ceria samples prepared by various methods. The relative area in percentage of the reduction peaks corresponding to surface Ce^{4+}-O^{-}-Ce^{4+} and Ce^{4+}- O^{-}-Ce^{3+} type species is also plotted. The plot clearly indicates the surface enrichment of defective Ce^{4+}- O^{-}-Ce^{3+} type species in the case of ceria samples prepared by alcoholysis method.

Proposed reaction mechanism:



Scheme S1. Catalytic pathway for the oxidative dehydrogenation of ethylbenzene using N_2O as oxidant and ceria as the catalyst.