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Inverse Opal Ceria-Zirconia: Architectural Engineering for Heterogeneous Catalysis

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Supplementary Information

Materials: $Ce_{0.5}Zr_{0.5}O_2$ powder was prepared by a modification of Hirano's method.[21] Equal molar ratios of $ZrOCl_2$ (Sigma Aldrich) and $(NH_4)_2Ce(NO_3)_6$ (Sigma Aldrich) were dissolved in deionized water to make a 0.005 molar (Ce + Zr) solution. The solution was reduced almost to the point of dryness on a hotplate. The resulting solid was then resuspended in deionized water for use in the preparation of an inverse opal. The non-templated material was obtained by collecting the dried solid and heat-treating at 550 °C for one hour.

The polystyrene opals were fabricated in alumina crucibles by a repeated sedimentation/evaporation process. Polystyrene beads (Duke Scientific, 1.0 μm) were received as a suspension in an aqueous solution. The beads were centrifuged and half of the water volume was removed prior to use. Once the polystyrene bead solution was of the desired thickness in the alumina crucible (approximately 3 mm), the polystyrene solution was placed into a 60 °C oven for 4 hours to remove the remaining water. An appropriate amount of the ceria-zirconia sol was added to the opal structure and the crucible was placed in an ultrasonicator for 5 minutes. The structure was then heat treated at 550 °C for 60 minutes, using a ramp rate of 1 °C min^{-1}.

Characterization: The SEM images were obtained using a JEOL JSM-6700F field emission SEM (accelerating voltage: 5 kV). The associated energy dispersive X-ray spectrometer (EDS, INCA energy dispersion X-ray microanalysis system, Oxford Instruments) was used to evaluate the residual Cl content. The X-ray diffraction pattern was collected using an

PANalytical X'Pert Pro Powder Diffractometer (tube: 45 kV, 40 mA, $CuK\alpha_{1,2}$, θ compensating divergence slit: automatic). The BET surface area measurements were performed using a Micromeritics ASAP 2010.

Catalytic Reactions: Catalytic activity was measured by flowing the reactant gas mixture through the catalyst material and characterizing the product gas. Experiments were carried out in a 10 mm diameter continuous flow quartz reactor using 50 mg of catalyst material. An additional 1.5 g of SiO_2 (quartz sand) was added on top of the catalyst. The reactor was placed inside a furnace and experiments performed at temperatures between 200 and 500 ºC, with data collected upon heating. Reduction was performed in-situ at 500˚C for 60 minutes with H_2 flow rate at 10 sccm and He at 40 sccm. This was followed by a 30 minute helium purge at a flow rate of 100 sccm (also at 500 ˚C).

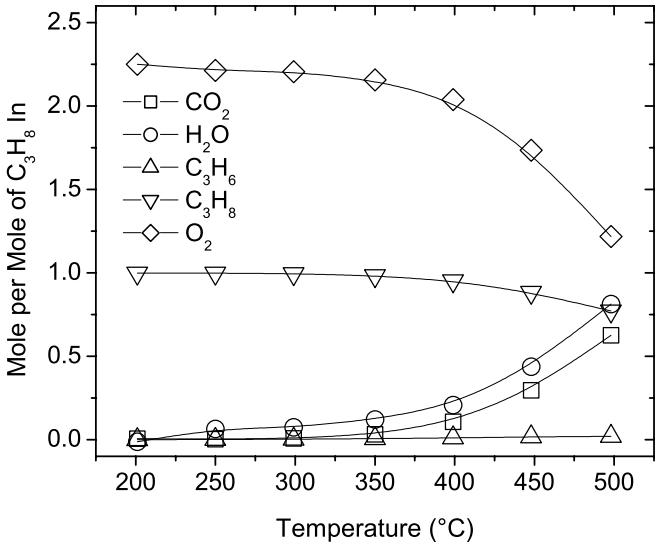
Aera FC-D980C digital mass flow controllers were used to regulate the amount and composition of the feed gas: 1.00 sccm for C_3H_8, 2.25 sccm for O_2 and 126.75 sccm for He. This particular composition was selected because of its demonstrated suitability for operation of so-called single chamber fuel cells.[1] Reactor pressure was maintained at 1.2 atm and the catalyst temperature was monitored using a thermocouple enclosed in a separate quartz tube placed in the middle of the catalyst bed. With such low flow rates, the temperature rise in the reactor was minimal (< 3 °C) and the system essentially isothermal.

The product gas composition was measured using a Varian CP-4900 micro gas chromatograph, equipped with a PoraPlot Q and Molecular Sieve 5A column. The catalyst was allowed to stabilize for 30 minutes at each testing condition before recording the gas composition. The concentrations of O_2, CO, CO_2, C_3H_8, C_3H_6, C_2H_6, C_2H_4 and CH_4 were

measured directly. The H_2O concentration was obtained from an oxygen balance, which then allowed the determination of the H_2 from a hydrogen balance.

The catalyst longevity test was performed at a catalyst temperature of 550 ºC with the following feed gas composition: 4.50 sccm for C_3H_8, 10.10 sccm for O_2 and 180.00 sccm for He.

1. Z. Shao, S. M. Haile, J. Ahn, P. D. Ronney, Z. Zhan and S. A. Barnett, *Nature*, 2005, **435**, 795-798.



Supplementary Figure 1. Product gas composition for propane oxidation over $Ce_{0.5}Zr_{0.5}O_2$ macroporous inverse opals. Concentrations are reported only for those gases present at levels above the detection limit. $P_{C_3H_8}$ = 0.009 atm, P_{O_2} = 0.021 atm, balance He, total flow rate = 130 sccm.