

## Supporting Information

### Exploration of atomic interface with inherent oxygen vacancy in zirconia for toluene oxidation

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## 1. Catalyst Characterization

The crystalline structure of the samples was determined by a D/max 2500 X-ray powder diffractometer equipped with Cu K $\alpha$  radiation. The tube voltage and current were set to 40 kV and 200 mA, respectively. Before sample loading, the sample table and cover glass were wiped clean with alcohol. An appropriate amount of powdered samples were selected and placed in the groove of the sample table, and the cover glass were pressed to evenly spread in the groove. The scanning range of 2 theta angle was changed from 10 ° to 80 ° with the scan rate of 5 °/min. The BET surface area was measured via a nitrogen physisorption method using an autosorb-iQ instrument at 77 k. The Brunauer-Emmet-Teller (BET) method was applied to obtain the specific surface area of the catalysts. In order to remove impurity molecules, the measured samples were weighed and degassed in He atmosphere at 150 °C for 2 h. The adsorption and desorption experiments were carried out in liquid nitrogen. The pore size distribution and total pore volume were also calculated using the Barrett-Joyner-Halenda (BJH) method. Raman spectra measurements were operated on a Lab-RAM Aramis Raman Spectrometer (HORIBA Jobin Yvon S.A.S.) with an excitation laser of 532 nm. The scan range was set to 100-1500 cm<sup>-1</sup>, and the instrument was calibrated with standard silicon wafer before testing. The high-resolution transmission electron microscopy (HRTEM) was obtained using a JEM-2100F. The acceleration voltage was set to 200kV. The sample preparation process was as follows: an appropriate amount of samples were evenly dispersed in ethanol by ultrasonic treatment and then dropped onto ultra-thin carbon film, which was used until ethanol was completely volatilized. The valences of different elements on the surface of the samples were tested by X-ray photoelectron spectroscopy (XPS) analysis on ESCALAB250XI using Al K $\alpha$  X-ray source. The C 1s peak at 284.8 eV was used as reference for the calibration of binding energies. The X-ray absorption spectra of Ce L<sub>3</sub>-edge were measured at the 4B9A beamline of Beijing Synchrotron Radiation Facility (BSRF).

The reducibility of the samples were measured via H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR) with a Micromeritics AutoChem II 2920 apparatus. Typically, 100

mg of catalyst was loaded in a tubular quartz reactor. The samples were preheated in a He flow at 300°C for 30 min to remove carbonate species from their surfaces, and then cooled down to 50°C. The H<sub>2</sub>-TPR spectra were recorded, while heating the temperature from 50°C to 800°C (10°C /min) in 10% H<sub>2</sub>/Ar flow. For O<sub>2</sub> temperature programmed desorption (O<sub>2</sub>-TPD), 200 mg samples were pretreated at 300°C in a pure helium atmosphere for 30 min, and then converted into 5% O<sub>2</sub>/He for 1 h. After cooling down to 50°C, He flow was switched into the samples to eliminate the excessive oxygen and maintained for 30 min. The O<sub>2</sub>-TPD profile was monitored with a mass spectrometer detector (Hiden DECRA) with increasing the temperature from 50 °C to 700 °C (5 °C /min) under He atmosphere.

The in situ diffuse reflectance FTIR spectra (DRIFTS) were recorded on a Nicolet iS50 spectrometer in the range of 1000-4000 cm<sup>-1</sup> with 32 scans at a resolution of 4 cm<sup>-1</sup>. Prior to the measurements, the samples were pretreated in N<sub>2</sub> flow (100 ml/min) at room temperature for 30 min and then at 250 °C for 1 h. The background spectrum was subtracted from each spectrum, respectively. After that, the mixture flow (1000 ppm toluene + 20% O<sub>2</sub> + N<sub>2</sub> balanced) was introduced and the spectra of samples at 250, 300, 350 and 400 °C were collected.

## 2. Computational method

Vienna Ab Initio Package (VASP) were employed to perform all the density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the PBE formulation.<sup>1</sup> Projected augmented wave (PAW) potentials were chosen to describe the ionic cores and the valence electrons were taken into account using a plane wave on basis with a kinetic energy cutoff of 400 eV.<sup>2, 3</sup> Partial occupancies of the Kohn-Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent, when the energy change was smaller than 10<sup>-5</sup> eV. A geometry optimization was considered convergent, when the force change was smaller than 0.02 eV/Å. Grimme's DFT-D3 methodology was used to describe the dispersion interactions.<sup>4</sup>

The equilibrium lattice constants of monoclinic ZrO<sub>2</sub> unit cell were optimized, when using a 7×7×7 Monkhorst-Pack k-point grid for Brillouin zone sampling, to be a=5.084

Å,  $b=5.233$  Å,  $c=5.233$  Å,  $\alpha=90^\circ$ ,  $\beta=99.03^\circ$ ,  $\gamma=90^\circ$ . We then use it to construct a m-ZrO<sub>2</sub>(-111) surface model (model 1) with  $p$  ( $2\times 2$ ) periodicity in the x and y directions and 3 stoichiometric layers in the z direction separated by a vacuum layer in the depth of 15 Å in order to separate the surface slab from its periodic duplicates. Model 1 comprises of 48 Zr and 96 O atoms. In another model (model 4), a Ce<sub>7</sub>O<sub>14</sub> cluster resides onto model 1. During structural optimizations, the  $\Gamma$  point in the Brillouin zone was used for k-point sampling, and the bottom two stoichiometric layers were fixed while the rest were allowed to relax.

The equilibrium lattice constants of tetragonal ZrO<sub>2</sub> unit cell were optimized, when using a  $9\times 9\times 7$  Monkhorst-Pack k-point grid for Brillouin zone sampling, to be  $a=3.579$  Å,  $c=5.160$  Å. We then use it to construct a t-ZrO<sub>2</sub>(011) surface model (model 3) with  $p$  ( $3\times 2$ ) periodicity in the x and y directions and 3 stoichiometric layers in the z direction separated by a vacuum layer in the depth of 15 Å in order to separate the surface slab from its periodic duplicates. One Zr atom on the outmost layer was replaced by one Ce atom. Model 3 comprises of 35 Zr, 1 Ce and 72 O atoms. In another model (model 3), one O atom by the Ce atom on the outmost layer of model 3 was removed in order to form an oxygen vacancy. During structural optimizations, the  $\Gamma$  point in the Brillouin zone was used for k-point sampling, and the bottom two stoichiometric layers were fixed while the rest were allowed to relax. The adsorption energy ( $E_{\text{ads}}$ ) of adsorbate A was defined as:

$$E_{\text{ads}} = E_{\text{A/surf}} - E_{\text{surf}} - E_{\text{A(g)}}$$

where  $E_{\text{A/surf}}$ ,  $E_{\text{surf}}$  and  $E_{\text{A(g)}}$  is the energy of adsorbate A adsorbed on the surface, the energy of clean surface, and the energy of isolated A molecule in a cubic periodic box with a side length of 20 Å and a  $1\times 1\times 1$  Monkhorst-Pack k-point grid for Brillouin zone sampling, respectively. Therefore, a negative value means exothermic adsorption. The more negative the adsorption energy, the stronger the adsorption.<sup>5</sup>

### 3. Results

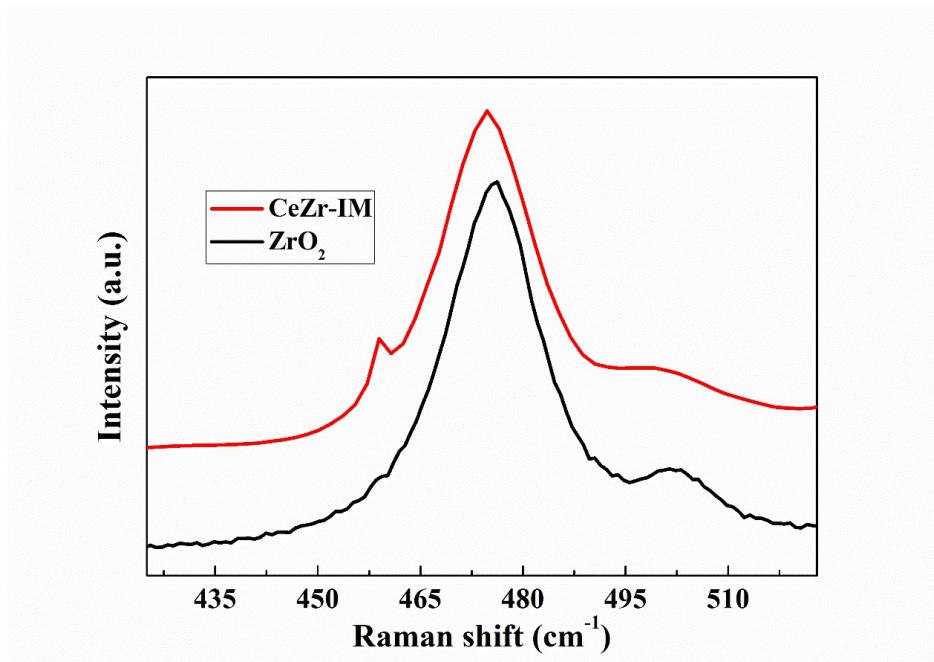


Fig. S1. Partially enlarged profile of Raman spectra of ZrO<sub>2</sub> and CeZr-IM catalysts.

### References

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