Controllably Engineering Surface Oxygen Defects on Bi$_2$Zr$_2$O$_7$ Compound for Catalytic Soot Combustion by Adjusting the Preparation Methods

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1. Catalyst characterization

The Powder X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Focus diffractometer instrument operating at 40 kV and 30 mA, with Cu target Kα-ray irradiation (\(\lambda = 1.5405 \text{ Å}\)). Scans were taken with a 2θ range from 10–90° and a step of 2° min\(^{-1}\). To keep the data comparable, all the samples were tested continuously.

\(\text{N}_2\) adsorption-desorption experiments of the samples were performed at 77 K on ASAP-2020 instrument. The specific surface areas of the catalysts were calculated using the Brunauer-Emmett-Teller (BET) method in the relative pressure (\(P/P_0\)) range of 0.05-0.25. The pore size distribution of the samples was calculated with the Barrett-Joyner-Halenda (BJH), and the average pore sizes were obtained from the distribution curves. The average pore volumes were accumulated at a relative pressure of \(P/P_0 = 0.99\).

Raman spectra of the catalysts were measured by using an excitation wavelength of 532 nm in Renishaw in Via instrument equipped with an Ar laser excitation source. The scanned Raman shift range is from 200 to 1400 cm\(^{-1}\).

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded on a TecnaiTM F30 transmission electron microscope. Elemental phase mapping and surface scans were also obtained by energy-dispersive spectroscopy (EDX) using the TecnaiTM F30 microscope equipped with an Oxford EDX detector operated at 300 keV.

Hydrogen temperature programmed reduction (H\(_2\)-TPR) experiments were carried out on FINESORB 3010C instrument. Generally, 50 mg catalyst was used for a test. Before the experiments, the catalysts were pretreated in 99.9% air flow at 120 °C for 30 min to remove any possible surface impurities. After purging with an 99.99% Ar flow at room temperature for 30 min, it was then increased from room temperature to 700 °C with a ramp of 10 °C min\(^{-1}\) in a 30 mL min\(^{-1}\) 10% H\(_2\)/Ar gas mixture flow. A thermal conductivity detector (TCD) was employed to monitor the H\(_2\) uptake. To quantify the H\(_2\) consumption amount, a 99.99% CuO sample was used as the calibration standard.

Soot temperature-programmed reduction (soot-TPR) experiments were conducted by using a DAS-7000 multiple adsorption instrument that was equipped with a TCD detector. Typically, 55
mg sample, which was prepared by uniform mixing of 5 mg soot with 50 mg catalyst powder, was placed in a quartz reactor. Prior to the test, it was treated in 99.99% Ar flow for 60 min at 120 °C to remove any physically adsorbed impurities. Afterwards, soot-TPR was carried out from 50 to 600 °C at a heating rate of 10 °C min⁻¹ in 30 mL min⁻¹ 99.99% He flow.

O₂ temperature-programmed desorption (O₂-TPD) measurements were carried out on Micromeritics Auto Chem 2920 chemical adsorption instrument with a TCD. Typically, 50 mg sample was placed in a quartz reactor, which was pretreated in a 30 mL min⁻¹ 99.99% Ar flow at 400 °C for 60 min. Afterwards, the sample was cooled down to 50 °C and saturated in a 10% O₂+He flow with a rate of 30 mL min⁻¹ for 1 h, which was followed by purging with a 30 mL min⁻¹ 99.99% He flow for 30 minutes to remove any physically adsorbed O₂. Temperature-programmed desorption experiments were then carried out from 50 to 800 °C with a heating rate of 10 °C min⁻¹ in a 30 mL min⁻¹ 99.99% He flow.

In situ DRIFTS experiments were conducted on a Bruker FTIR spectrometer equipped with an in situ diffuse reflectance pool and an MCT detector cooled by liquid nitrogen. Typically, a spectroscopy was collected in a range of 600–4000 cm⁻¹ at 300 °C with 32 scans accumulated, and under desired gas atmosphere.

The EPR experiment was performed on JEOL FA-200 EPR spectrometer, which works in a field of 100 kHz and a microwave frequency of 9.06 GHz. After the catalysts were pretreated in an oxygen atmosphere at 350 °C and 100 Torr for 1 hour, they were cooled to room temperature, and then a 10% O₂/Ar gas mixture flow was introduced. After the surface was saturated and the oxygen species was captured at liquid nitrogen temperature of 77 K, it was then raised to room temperature for signal collection.

The FTIR spectra were recorded in the range of 4000-400 cm⁻¹ using a Bruker Vertex equipped with an MCT detector. Prior to the measurements the samples were homogenized with KBr by using an agate mortar, and then pressed into thin and transparent pellets.

X-ray Photoelectron Spectroscopy (XPS) tests were performed with a PerkinElmer PHI1600 system using a single Mg Kα X-ray source operating at 300 W and 15 kV. The spectra were obtained at ambient temperature using ultra-high vacuum. The binding energies were calibrated by using the C 1s peak of graphite at 284.8 eV as the standard.
2. Activity evaluation

Temperature programmed oxidation (TPO) technique was used to evaluate the activity of the prepared catalysts for soot combustion by using a FINESORB-3010C multiple adsorption instrument (Finetec, China). Tests were carried out in a fixed-bed quartz tube micro-reactor with an inner diameter of 6 mm. To evaluate the activity of a catalyst under tight contact condition, typically, 5 mg soot (Printex-U, diameter of 25 nm, purchased from Degussa) was mixed with 50 mg catalyst powder and grounded for 10 min. Before loading into the reactor, the grounded mixture was diluted by 100 mg inert silica with a soot/catalyst/silica weight ratio of 1/10/20 to avoid the formation of hot spots during the activity test. A K-type thermocouple was used to monitor the temperature of the catalyst bed accurately with the thermocouple head point touching the catalyst bed. To measure the reaction behaviors of the catalysts, all data were collected with the increasing of the temperature to 800 °C at a rate of 10 °C min\(^{-1}\). The volume composition of the feed gas is 10% O\(_2\) and balanced by 99.9% Ar, with a flow rate of 30 ml min\(^{-1}\). A QMS-1800 mass spectrometer (Finetec, China) was used to detect the products. The mass spectrum signal m/z = 44 and 28 was used to monitor the generation of CO\(_2\) in the exhaust gas, and m/z = 28 and 16 is used to detect the generation of CO in the exhaust gas.

Since the CO\(_2\) molecules are able to split into m/z= 28 fragments, which is overlapped with the main CO signal, the quantification of CO amount needs to subtract the contribution from CO\(_2\). First, with 5 injections of pure CO\(_2\) under the same condition, an average splitting ratio f (f = A\(_{28}\)/A\(_{44}\)) was obtained to calculate the contribution of the m/z = 28 fragments from CO\(_2\). Then, at a certain temperature, the accurate relative amount of CO product (A\(_{CO}\)) can be defined as A\(_{T-CO}\) = A\(_{28}\) – A\(_{44}\) × f, and the accurate relative amount of CO\(_2\) product (A\(_{CO2}\)) can be defined as A\(_{T-CO2}\) = A\(_{44}\) × (1 + f). Similarly, for a complete TPO reaction, the totally released amount of CO\(_2\) (A\(_{Max-CO2}\)) and CO (A\(_{Max-CO}\)) can be defined in the same way. Therefore, the conversion of soot particles (X\(_{soot}\)) and the CO\(_2\) selectivity at a certain temperature can be calculated by the formula (1) and (2) in sequence:
\[
X_{\text{soot}} = \frac{A_{T-C0} + A_{T-CO2}}{A_{\text{Max}}-C0 + A_{\text{Max}}-CO2} \times 100\% \quad (1)
\]

\[
S_{CO2} = \frac{A_{\text{Max}}-CO2}{A_{\text{Max}}-CO2 + A_{\text{Max}}-CO} \times 100\% \quad (2)
\]

The soot combustion in the presence of NO\textsubscript{x} was measured on the same instruments, and the mixture of 5 mg soot and 50 mg catalysts was treated in a feed with the 500 ppm NO + 5% O\textsubscript{2} and balanced with 99.9% Ar. The same QMS-1800 mass spectrometer was used to detect the products.

Isothermal reactions were studied with the mixture of 20 mg Bi\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} catalyst and 2 mg soot particles at 330 °C, at which the soot conversion can be controlled <20% on all the samples, thus being able to achieve data in a kinetic regime. The tests were conducted in a quartz reactor with a 10% O\textsubscript{2}/Ar flow (100 mL min\textsuperscript{-1}). In this way, the reaction rates (R\textsubscript{w} and R\textsubscript{s}) over all the catalysts for soot combustion can be calculated from the slope of the lines. The number of soot reactive oxygen sites (O\textsuperscript{*}) is quantified through the combination of soot–TPR and H\textsubscript{2}–TPR techniques. The turnover frequency (TOF) of the catalysts, which reflects the intrinsic activity, was calculated through dividing the reaction rates (R\textsubscript{w}) by the amount of soot reactive oxygen sites (O\textsuperscript{*}), as expressed here with the equation of TOF = R\textsubscript{w}/O\textsuperscript{*}. 

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3. Supplementary results

Fig. S1. Soot combustion over the catalysts under loose contact condition. (a) soot conversion profiles, (b) TPO-MS profiles; (c) Soot combustion profiles over the 1% Pd/Al₂O₃ catalyst under tight contact condition.
Fig. S2. N$_2$ adsorption-desorption profiles of the Bi$_2$Zr$_2$O$_7$ catalysts. (a) Isotherms; (b) pore size distribution profiles.
Fig. S3. (a) $\text{H}_2$-TPR profiles and (b) $\text{O}_2$-TPD profiles of the pure $\text{Bi}_2\text{O}_3$ sample.
Fig. S4. XPS C 1s signal of the Bi$_2$Zr$_2$O$_7$ catalysts.
Fig. S5. XPS spectra of the Bi$_2$Zr$_2$O$_7$ catalysts. (a) Bi 4f; (b) Zr 3d.