

Cite this: *Catal. Sci. Technol.*, 2025, 15, 3298

Enhancing the low-temperature performance of Pt-based three-way catalysts using CeO₂(core)@ZrO₂(shell) supports†‡

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Developing robust Pt/CeO₂-based three-way catalysts (TWCs) with enhanced oxygen buffering capability and low-temperature activity is highly desirable. In this study, a new TWC family, Pt/(1 - x)CeO₂(core)@xZrO₂(shell) (where x = 0–0.5), was prepared and evaluated at degreened (DG) and hydrothermally aged (HTA) states. Incorporation of 0.1 molar concentration of ZrO₂ resulted in a decreased temperature that 50% (T₅₀) (CO: 167 °C, THC_s: 218 °C, NO: 228 °C) and 90% (T₉₀) (CO: 207 °C, THC_s: 237 °C, NO: 244 °C) conversions achieved over HTA 1.8 wt% Pt/0.9CeO₂@0.1ZrO₂ compared to the HTA 1.8 wt% Pt/CeO₂ sphere (CO: T_{50,90} = 179, 222 °C, THC_s: 234, 252 °C, NO_x: 240, 260 °C). An enhanced oxygen storage capacity and oxygen release rate were observed over Pt/0.9CeO₂@0.1ZrO₂ compared to the Pt/CeO₂ sphere. Increasing the ZrO₂ molar concentration to values greater than 0.2 resulted in increased T₅₀s (224, 265 274 °C) and T₉₀s (251, 289, 292 °C) for CO, THC_s, and NO_x, respectively, over 1.8 wt.% Pt/0.5CeO₂@0.5ZrO₂. Overall, this work highlights the potential of forming a ZrO₂ shell on CeO₂ spheres as a support for TWC applications.

Received 25th July 2024,
Accepted 11th March 2025

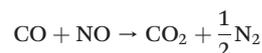
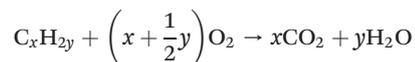
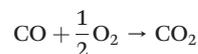
DOI: 10.1039/d4cy00921e

rsc.li/catalysis

1. Introduction

Three-way catalysts (TWCs) can simultaneously convert carbon monoxide (CO), hydrocarbons (HCs), and nitrogen oxides (NO_x) to less harmful products (CO₂, H₂O, N₂) and they are the key components for the control of stoichiometric spark ignition engine emissions.¹ TWCs are currently highly efficient when the vehicle emission temperature is higher than 350 °C. However, approximately 80% of vehicle

emissions are emitted to the atmosphere during the cold start period (first 1–3 min of vehicle operation) when the TWCs are not warm enough.² Moreover, the improved engine efficiency of vehicles operating on stoichiometric feed has led to low engine operating temperatures and lower exhaust temperatures. Low exhaust temperatures in gasoline aftertreatment systems necessitate the development of TWCs that are active at low temperatures.^{3–5} Specifically, the “150 °C challenge”⁶ aimed to achieve 90% conversion of CO, HCs, and nitrogen NO_x at temperatures as low as 150 °C. The most common commercial TWCs utilize platinum group metals (PGMs), such as Pd,⁷ Pd/Rh,^{8,9} Pt/Rh,^{10,11} and Pt/Pd/Rh,^{12,13} which can simultaneously convert CO, HCs, and NO_x to CO₂, H₂O, and N₂, respectively, *via* the following reaction routes:¹⁴



Pt-based TWCs have attracted significant attention due to the lower cost of Pt (\$956 per troy ounce; Jan. 2025) compared to Rh (\$4675 per troy ounce; Jan. 2025).¹⁵

The active metals are often dispersed on a support to maximize their active surface area. The rare earth metal

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4cy00921e>

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oxide, ceria (CeO_2), is of particular interest in TWCs because Ce exists in two oxidation states ($\text{Ce}^{4+}/\text{Ce}^{3+}$) under operating conditions.¹ The $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple allows CeO_2 to store/release O_2 through a redox reaction ($2\text{CeO}_2 \leftrightarrow \text{Ce}_2\text{O}_3 + 0.5 \text{O}_2$)^{16,17} under oxygen-rich/deficient conditions, respectively.^{18–20} The oxygen storage capacity (OSC) of CeO_2 is important in TWCs as it can buffer the oxygen-rich/deficient conditions resulting from the imprecise control of fuel injection in gasoline vehicles, leading to 1% oscillations for an air/fuel ratio of around 14.7 during vehicle operation.^{21,22} Oxygen-rich/deficient conditions can significantly impact the efficiency of TWCs to mitigate CO, HCs, and NO_x .^{12,23,24} Specifically, oxygen can be stored in CeO_2 under lean conditions and can be supplied to the oxidation reactions under rich conditions. Zirconium is typically incorporated into CeO_2 to increase its lattice oxygen mobility to further improve the TWC performance.^{25–27} For example, a more than an order of magnitude increase in OSC (from 25 to 350 $\mu\text{mol}_\text{O} \text{g}^{-1}$) was reported by increasing the Ce:Zr molar ratio from 0 (CeO_2) to 1 ($\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$).²⁵ Moreover, the CO and NO_x catalytic activity over Pd/ CeO_2 - ZrO_2 - Pr_2O_3 with various Ce:Zr ratios revealed that a higher OSC (488.4 $\text{mol}_\text{O} \text{g}^{-1}$) was responsible for a wider operational window (100% CO conversion at $\lambda \geq 0.925$ and 100% NO conversion at $\lambda \leq 1.075$).²⁶

Although CeO_2 possesses high OSC, it can suffer from sintering when exposed to elevated temperatures. For instance, TWCs can be exposed to 900–950 °C during deceleration fuel cut-offs, scavenging, and disabled fuel enrichment at high engine loads.²⁸ Polyhedral CeO_2 , commonly used in catalytic reactions,^{29–31} loses the majority of its surface area when exposed to elevated temperatures. Specifically, the surface area of polyhedral CeO_2 is decreased from 89 to 21 $\text{m}^2 \text{g}^{-1}$ when increasing the calcination temperature from 450 to 600 °C.³² Therefore, CeO_2 supports that can maintain their surface area after exposure to elevated temperatures attract a lot of interest. Several strategies have been adopted to enhance the thermal stability of CeO_2 . In a study by Chen *et al.*, CeO_2 islands were anchored onto the surface of penta-site rich Al_2O_3 leading to smaller CeO_2 crystalline sizes (~11–17 nm) than the bare CeO_2 sample (~22 nm) after hydrothermal aging.¹ Other methods include the incorporation of ZrO_2 to the CeO_2 lattice to form ceria-zirconia solid solutions.³² Herein, an approach of coating CeO_2 nanospheres with a ZrO_2 shell is studied by synthesizing $(1-x)\text{CeO}_2@x\text{ZrO}_2$ ($x = 0, 0.1, 0.2, 0.3, 0.5$) supports for TWC applications. The TWC activity and hydrothermal stability of Pt/ $(1-x)\text{CeO}_2@x\text{ZrO}_2$ catalysts were evaluated using the U.S. DRIVE test protocol.³³ High-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), and energy dispersive X-ray spectroscopy (EDS) were conducted to reveal the morphology of $(1-x)\text{CeO}_2@x\text{ZrO}_2$. Moreover, CO-pulse chemisorption and CO diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS) were conducted to identify the Pt dispersion. X-ray photoelectron

spectroscopy (XPS) was used to determine the Ce oxidation states. Finally, complete oxygen storage capacity (OSCC) and oxygen release rate (ORR) measurements were conducted to elucidate their effect on the TWC performance.

2. Experimental

2.1. Reagents and materials

Zirconium(IV) butoxide ($\text{Zr}(\text{BuO})_4$) solution (80 wt% in 1-butanol, Sigma-Aldrich), anhydrous ethanol (EtOH, 200 proof, Decon), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) (Fisher Scientific, 99.99%), ammonium hydroxide (NH_4OH , 28–30 wt% solution of NH_3 in water, Sigma-Aldrich), 2,2,4-trimethylpentane (*i*- C_8H_{18}) (Sigma Aldrich, 99.8%), and silicon carbide (SiC) (Alfa Aesar, $\geq 98\%$) were used as received. A Brij30 solution (100 wt%, Acros Organics, purity 99.79%) was diluted with D.I. water to a 3.8 wt% Brij30 solution prior to usage. Cerium(III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (Sigma Aldrich, 99.999%), zirconium(IV) oxynitrate hydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$) (Sigma Aldrich, 99%), and tetraammineplatinum nitrate ($\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$) (STREM Chemicals, 99%) were diluted with D.I. water to form 0.1 M, 0.5 M $\text{Ce}(\text{NO}_3)_3$, 0.1 M $\text{ZrO}(\text{NO}_3)_2$, and 0.015 M $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ solutions prior to usage. D.I. water with a resistivity of 18.2 $\text{M}\Omega \text{cm}$ was used for all the syntheses in this study.

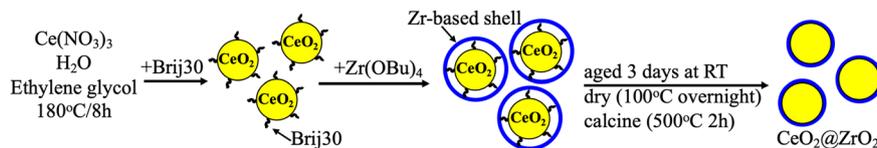
2.2. Catalyst synthesis

CeO_2 spheres were prepared by a hydrothermal synthesis method (Scheme 1).³⁴ Briefly, CeO_2 spheres were synthesized by mixing 5.2 mL of 0.5 M $\text{Ce}(\text{NO}_3)_3$ solution with 78 mL ethylene glycol and the obtained solution was stirred for 4 h. The mixture was then transferred to an autoclave fitted with a Teflon liner and heated to 180 °C for 8 h, followed by cooling down to room temperature. The obtained mixture was centrifuged at 5000 rpm for 20 min and the solid phase was redispersed in D.I. water and centrifuged three times. The solid phase was subsequently redispersed in anhydrous EtOH and centrifuged three times. The retrieved solid phase was then dried (110 °C/overnight) and calcined (500 °C/2 h) to obtain CeO_2 spheres.

$(1-x)\text{CeO}_2@x\text{ZrO}_2$ supports were synthesized using CeO_2 spheres (dispersed in anhydrous EtOH). Briefly, CeO_2 spheres were dispersed in 39 g anhydrous EtOH, followed by the addition of 0.13 mL of 3.8 wt% Brij 30 solution under constant stirring at room temperature. The solution was stirred for an hour, followed by the addition of 0.132, 0.297, 0.509, and 1.189 mL of 0.1 M $\text{Zr}(\text{BuO})_4$, followed by overnight stirring to synthesize $(1-x)\text{CeO}_2@x\text{ZrO}_2$ with $x = 0.1, 0.2, 0.3, 0.5$, respectively. The solution was centrifuged and redispersed in 50 mL D.I. water. This step was repeated four times. The solution was then aged for 3 days at room temperature. The solid phase was separated, followed by drying (110 °C/overnight) and calcination (500 °C/2 h).

The reference $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ solid solution support was synthesized by co-precipitation as reported previously³² for an immediate comparison with $0.9\text{CeO}_2@0.1\text{ZrO}_2$. Briefly, 72





Scheme 1 Synthesis procedure of $\text{CeO}_2@\text{ZrO}_2$ supports.

mL of 0.1 M $\text{Ce}(\text{NO}_3)_3$ solution and 8 mL of 0.1 M $\text{ZrO}(\text{NO}_3)_2$ solution were mixed, resulting in a Ce/Zr precursor solution. This Ce/Zr precursor solution was added dropwise into 48 mL of NH_4OH under stirring. The solution was stirred for 30 min. The formed precipitant was washed with 50 mL D.I. water followed by vacuum filtration. The obtained solids were dried (110 °C/overnight) and calcined (500 °C/2 h).

1.8 wt% Pt was deposited to $(1-x)\text{CeO}_2@x\text{ZrO}_2$ ($x = 0.1, 0.2, 0.3, 0.5$) and $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ by wet-impregnation. Specifically, 6.3 mL of 0.015 M $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ solution was added to 1 g of $(1-x)\text{CeO}_2@x\text{ZrO}_2$ and $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ supports. The liquid was evaporated under stirring at room temperature, followed by drying (110 °C/overnight) and calcination (500 °C/2 h).

2.3. Material characterization

The Brunauer–Emmett–Teller (BET) surface areas of as-synthesized supports and catalysts were determined by nitrogen physisorption with a Micromeritics Tri-Star II surface area analyzer.

The morphology of $(1-x)\text{CeO}_2@x\text{ZrO}_2$ ($x = 0$ and 0.3) supports was determined by HRTEM, STEM, and EDS techniques. HRTEM images were obtained at an accelerating voltage of 200 kV using a JEM-2010 equipment. The powdered samples were dispersed in anhydrous EtOH (HRTEM) and isopropyl alcohol (STEM, EDS) followed by ultrasonication. The obtained mixture was then added dropwise onto carbon-coated copper grids (Electron Microscopy Sciences, CF300-CU) followed by drying in air at room temperature. STEM images and EDS elemental maps of individual particles were collected using an FEI Talos F200X.

X-ray diffraction (XRD) patterns of $(1-x)\text{CeO}_2@x\text{ZrO}_2$ ($x = 0, 0.1, 0.2, 0.3, 0.5$) supports were collected using a Rigaku Ultima IV with a $\text{Cu K}\alpha$ X-ray source. The data were collected from $2\theta = 10$ to 90° with a step size of 0.02° and scan speed of 2°min^{-1} .

CO-pulse chemisorption experiments were conducted using a Micromeritics AutoChem II 2920 equipped with a thermal conductivity detector. An approximately 50 mg sample was loaded in a U-shaped quartz tube reactor. The catalysts were initially oxidized with 20% O_2/Ar at 500 °C for 30 min. The catalysts were then cooled down to 250 °C in Ar, followed by purging with Ar for 30 min to remove physisorbed O_2 . The catalysts were then reduced with 10% H_2/Ar for 30 min at 250 °C followed by purging with Ar for another 30 min to remove physisorbed H_2 . The reactor was immersed in a dry ice–ethanol mixture and cooled to -78°C

under a He flow to prevent CO adsorption on CeO_2 .³⁵ CO pulses (10% CO/He, 0.5 cm^3) were injected every 5 min until no CO consumption was observed. The total flow rate for the CO-pulse chemisorption experiment was maintained at 50 sccm ($\text{cm}^3 \text{min}^{-1}$ (STP)). The Pt particle size was calculated assuming all particles were equally sized hemispheres and a stoichiometry of $\text{CO}/\text{Pt} = 1$ was assumed.³⁶

CO-DRIFTS experiments were performed as reported previously³⁷ using a Nicolet iS50 FTIR spectrometer (Thermo Fisher) equipped with a high temperature reaction chamber (Harrick Praying Mantis). An approximately 25 mg sample was loaded in a sample holder and it was initially pretreated in Ar at 200 °C for 30 min. The sample was then cooled down to 25 °C in Ar, where background spectra were collected at a resolution of 4 cm^{-1} and 32 scans. Samples were then exposed to 1% CO/Ar for 30 min, followed by purging with Ar for another 30 min to remove gas phase CO. The total flow rate for the CO-DRIFTS experiments was 100 sccm.

The OSCC and ORR were measured using the low-temperature TWC test protocol defined by U.S. DRIVE in a customized reactor setup described in section 2.4.³³ OSCC measurements on ~ 25 mg of degreened catalyst were performed isothermally from 550 °C to 350 °C to 150 °C. The catalysts were initially exposed to 1.5% O_2/Ar for 10 min, followed by switching to 0.2% CO/Ar for another 10 min. The switch from one gas stream to another was facilitated with an automated four-way valve for a smoother transition. Before exposure to O_2 at each steady-state temperature, the catalyst surface was purged with Ar for 30 min. The OSCC was calculated by integrating the CO consumption from 0 to 10 min and the ORR was calculated from the slope of the CO concentration vs. time plot between 6 and 9 s after 0.2% CO/Ar was introduced to the feed stream. CO ($m/z = 29$) and Ar ($m/z = 40$) signals were recorded with a Pfeiffer Omnistar GSD 320 mass spectrometer with a 200 ms interval.

XPS spectra were recorded on a Kratos Axis Ultra XPS spectrometer equipped with an Al $\text{K}\alpha$ (1486.6 eV) X-ray source at 200 W power and a pressure of 3.0×10^{-8} mbar. Survey scans were obtained between 0 and 1200 eV with a step size of 1 eV, a dwell time of 200 ms, and a pass energy of 140 eV averaged over 5 scans. Core-level region scans for Ce 3d, Zr 3d, C 1s, and O 1s were obtained at the corresponding binding energy ranges with a step size of 0.1 eV, an average dwell time of 260 ms, and a pass energy of 20 eV averaged over 5 scans. Data processing was performed using CasaXPS software employing Shirley-routine background subtraction and instrument-specific atomic sensitivity factors.



2.4. Catalyst evaluation

Catalyst evaluation was performed in a customized U-shaped quartz reactor, as reported previously.³⁸ Briefly, 100 mg of catalyst powder diluted with 200 mg SiC was placed in the reactor tube stabilized by two loosely packed quartz wool plugs. The reactor was then placed in a cylindrical furnace surrounded by quartz wool to eliminate heat gradients. A K-type thermocouple was inserted into the top quartz wool plug in the U-shaped reactor to record the inlet gas temperature. Another K-type thermocouple was attached outside the reactor at the same height as the inlet temperature thermocouple to allow the PID temperature controller to control the furnace temperature. The gases used to simulate the TWC performance were purchased from Airgas and were the following: 99.999% CO₂, 99.999% O₂ (UHP), 10.01% H₂/Ar, 10.1% CO/Ar, 1% NO/Ar, 5% C₂H₄/Ar, 5% C₃H₆/Ar, 1% C₃H₈/Ar, and 99.999% Ar (UHP). All gases were regulated by a set of MKS mass flow controllers. Liquid *i*-C₈H₁₈ was placed in a bubbler immersed in a controlled temperature (0 °C) water bath and gas phase *i*-C₈H₁₈ was carried by Ar to the reactor. The Clausius–Clapeyron equation and the vapor pressure of *i*-C₈H₁₈ (1.78 kPa at 0 °C)³⁹ were used to calculate the Ar flow required to carry *i*-C₈H₁₈ from the bubbler to the reactor. Water was supplied to the reactor (0.027 mL min⁻¹) by a D-series pump (Teledyne Isco) and steam was generated in a tube furnace set at 200 °C that was carried by Ar to the reactor. The catalytic performance experiments were conducted from 100 to 500 °C at a heating rate of 2 °C min⁻¹. The temperature was recorded every second using a LabView program. The total flow rate was maintained to 333 sccm, corresponding to a gas hourly space velocity of 142 500 h⁻¹. The reactor outlet gas was diluted with 1332 sccm Ar and analyzed using an MKS MultiGas 2030 FTIR gas analyzer operating at 191 °C. The reactor gas lines were heated at 170 °C to avoid water condensation.

Catalysts were evaluated after degreening (DG) and redox hydrothermal aging (HTA). Degreening of the catalysts was conducted at 700 °C for 4 h under 10% H₂O, 10% CO₂, Ar balance. Redox HTA was conducted at 800 °C for 10 h at a switching frequency of 0.1 Hz between a lean (5% O₂, 10% H₂O, 10% CO₂, Ar balance) and a rich (3% CO, 1% H₂, 10% H₂O, 10% CO₂, Ar balance) gas stream. Prior to evaluating the DG and HTA catalysts, the catalysts were pretreated at 600 °C (10% H₂O, 13% CO₂, Ar balance) for 20 min. Simulated TWC oxidation experiments were performed using the low temperature oxidation catalyst test protocol stoichiometric gasoline direct injection (S-GDI) gas composition defined by U.S. DRIVE³³ (13% CO₂, 10% H₂O, stoichiometric O₂, 1670 ppm H₂, 5000 ppm CO, 1000 ppm NO, 700 ppm C₂H₄, 1000 ppm C₃H₆, 300 ppm C₃H₈, 1000 ppm *i*-C₈H₁₈, hydrocarbons in C₁ basis, Ar balance).

3. Results and discussion

3.1. Surface characterization

The BET surface areas and N₂ adsorption/desorption isotherms of (1 - *x*)CeO₂@*x*ZrO₂ (where *x* = 0, 0.1, 0.2, 0.3,

and 0.5) and Ce_{0.9}Zr_{0.1}O₂ solid solution supports are summarized in Table S1 and Fig. S1,[†] respectively. All (1 - *x*)CeO₂@*x*ZrO₂ supports have surface areas of 69.3–95 m² g⁻¹ and type II isotherms, characteristic of non-porous or macroporous materials.⁴⁰ The solid solution Ce_{0.9}Zr_{0.1}O₂ has a surface area of 77.2 m² g⁻¹ and a type IV isotherm, characteristic of mesoporous materials.

The morphology of synthesized CeO₂ is spherical (Fig. S2[†]) with a uniform diameter of ~160 nm. Fig. 1(a, b and d) show the HRTEM image and EDS maps of the 0.7CeO₂@0.3ZrO₂ support. The EDS elemental maps of Ce and Zr suggest that the ZrO₂ overlayer covers the surface of CeO₂ uniformly. Fig. 1(c) shows that ZrO₂ is enriched in the shell layer of 0.7CeO₂@0.3ZrO₂, while the Ce signal is more dominant in the core and decreases when approaching the shell, suggesting that a core@shell structure was prepared. However, an uneven ZrO₂ coating was formed (Fig. S3[†]) when the Zr molar concentration increased from 0.3 (0.7CeO₂@0.3ZrO₂) to 0.5 (0.5CeO₂@0.5ZrO₂), attributed to excess ZrO₂ that cannot be coated evenly.

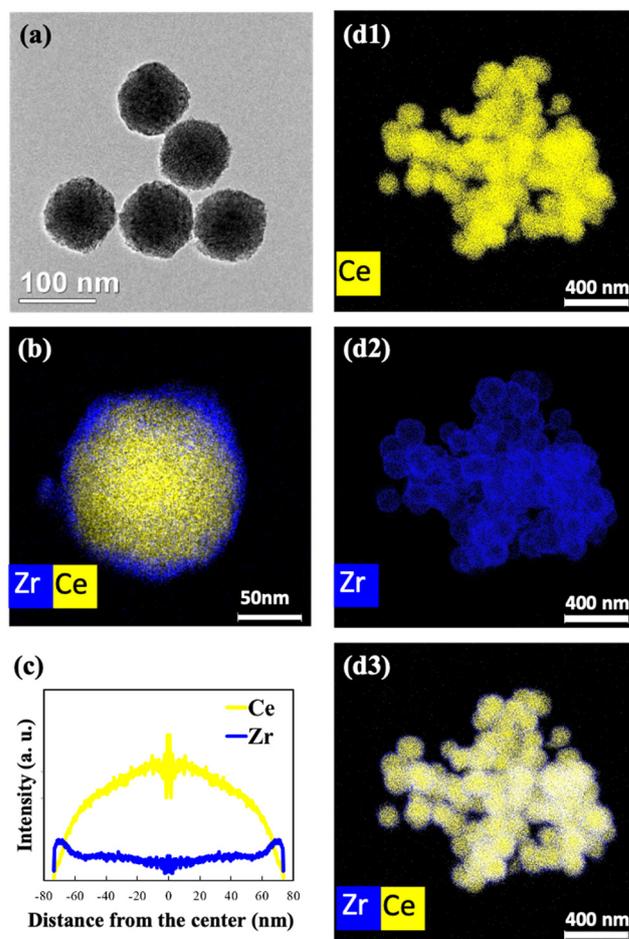


Fig. 1 (a) HRTEM image, (b and d) EDS elemental maps of Ce and Zr of the 0.7CeO₂@0.3ZrO₂ support and (c) Ce and Zr elemental distributions obtained by converting the brightness in intensity from the EDS elemental map in (b).



XRD spectra of the $(1-x)\text{CeO}_2@x\text{ZrO}_2$ supports (Fig. 2) show that CeO_2 spheres possess peaks at 2θ of 28.5° and 33.1° that correspond to the (111) and (200) planes of cubic CeO_2 , respectively.⁴¹ Increasing the Zr molar concentration to values ≥ 0.2 led to the appearance of additional peaks at 30.2 and 35.2° , which correspond to the (111) and (200) planes of tetragonal ZrO_2 , respectively.^{42,43}

The average Pt particle size and dispersion of 1.8 wt% Pt/ $(1-x)\text{CeO}_2@x\text{ZrO}_2$ were obtained by CO-pulse chemisorption (Fig. 3). The Pt/ CeO_2 sphere showed an average Pt particle size of 7.7 nm, corresponding to a Pt dispersion of 13.5%. Similar average Pt particle sizes and dispersions were observed over Pt/ $(1-x)\text{CeO}_2@x\text{ZrO}_2$ with $x \leq 0.2$. Specifically, the average Pt particle size of Pt/ $0.9\text{CeO}_2@0.1\text{ZrO}_2$ and Pt/ $0.8\text{CeO}_2@0.2\text{ZrO}_2$ was 6.8 nm (Pt dispersion: 15.4%) and 7.2 nm (Pt dispersion: 15.7%), respectively. The similar Pt particle size and dispersion observed at low Zr molar concentrations suggest the existence of strong metal-support interactions between Pt and CeO_2 .⁴⁴ An increase in Zr molar concentration to 0.3 and 0.5 in Pt/ $(1-x)\text{CeO}_2@x\text{ZrO}_2$ led to an increase in the average Pt particle size to 9.9 nm (Pt dispersion: 11.4%) and 14.3 nm (Pt dispersion: 7.9%), respectively.

CO-DRIFTS experiments conducted over Pt/ $(1-x)\text{CeO}_2@x\text{ZrO}_2$ catalysts (Fig. 4) showed that Pt/ $(1-x)\text{CeO}_2@x\text{ZrO}_2$ contains two types of Pt species. The high wavenumber peak (2097 cm^{-1}) is attributed to CO adsorbed on ionic Pt^{2+} strongly interacting with CeO_2 .^{45,46} The low wavenumber peak (2087 cm^{-1}) is attributed to CO adsorbed on Pt^0 particles.^{47,48} The 2097 cm^{-1} and 2087 cm^{-1} peaks are more pronounced at low ($x \leq 0.1$) and high ($x > 0.1$) Zr molar concentrations, respectively. This observation suggests that increasing the molar concentration of Zr can hinder the occurrence of Pt^{2+} species that can strongly interact with CeO_2 . Instead, Pt^0 particles are formed, consistent with the

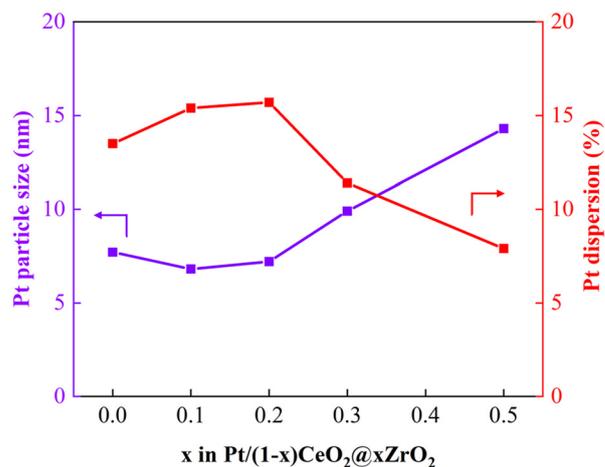


Fig. 3 Average Pt particle size and dispersion of 1.8 wt% Pt/ $(1-x)\text{CeO}_2@x\text{ZrO}_2$ catalysts obtained by CO-pulse chemisorption.

CO-pulse chemisorption results that show a decreased Pt dispersion with increasing Zr molar concentration.

The XPS survey of $0.9\text{CeO}_2@0.1\text{ZrO}_2$ (Fig. S4[†]) shows the presence of 16.6 atomic% of Zr, suggesting the successful deposition of ZrO_2 on the surface of $0.9\text{CeO}_2@0.1\text{ZrO}_2$. The XPS results for Ce 3d of the CeO_2 spheres and $0.9\text{CeO}_2@0.1\text{ZrO}_2$ supports are shown in Fig. 5. The peaks labeled V_o , V' , u_o , and u' correspond to Ce^{3+} and peaks labeled u , u'' , v , v'' , and v''' correspond to Ce^{4+} .⁴⁹ The peak area that belongs to Ce^{3+} is 13.0% and 17.2% for CeO_2 spheres and $0.9\text{CeO}_2@0.1\text{ZrO}_2$, respectively, suggesting that Zr incorporation leads to a higher $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio. It was reported that oxygen vacancies from nano-sized CeO_2 are associated with the presence of Ce^{3+} on the surface resulting in a higher $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio compared to bulk CeO_2 .⁵⁰ Therefore, the increase of $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio in $0.9\text{CeO}_2@0.1\text{ZrO}_2$ may result in a higher oxygen storage capacity and oxygen release rate (discussed in section 3.2).

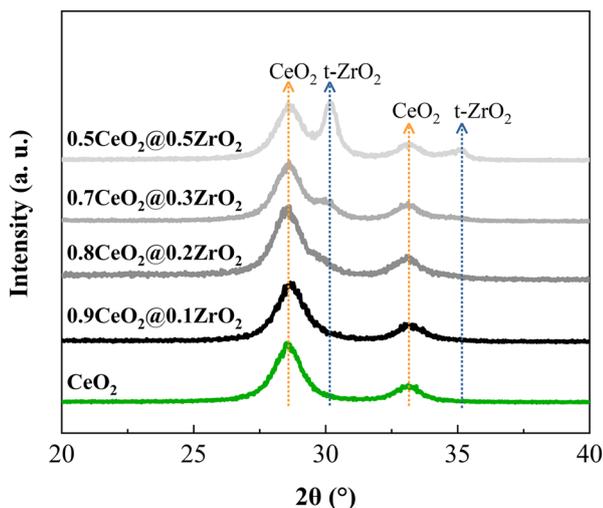


Fig. 2 XRD patterns of $(1-x)\text{CeO}_2@x\text{ZrO}_2$ ($x = 0, 0.1, 0.2, 0.3, 0.5$) supports (t: tetragonal).

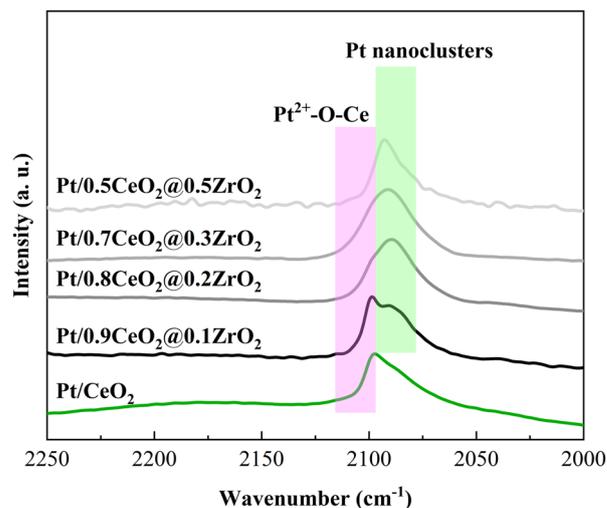


Fig. 4 CO-DRIFTS over fresh 1.8 wt% Pt/ $(1-x)\text{CeO}_2@x\text{ZrO}_2$ ($x = 0, 0.1, 0.2, 0.3, 0.5$) catalysts.



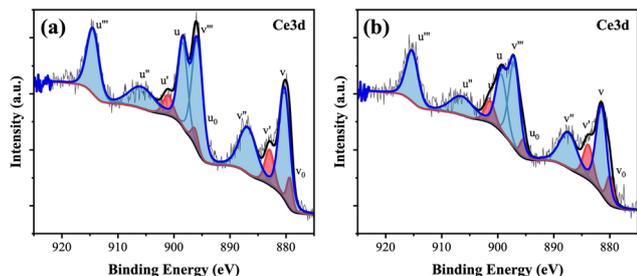


Fig. 5 XPS results for Ce 3d of (a) CeO_2 and (b) $0.9\text{CeO}_2@0.1\text{ZrO}_2$.

3.2. TWC performance

The temperatures that 50% and 90% CO, total HCs (THCs) and NO_x conversions achieved (T_{50} and T_{90} , respectively) over $\text{Pt}/(1-x)\text{CeO}_2@x\text{ZrO}_2$ (DG) catalysts are summarized in the bar chart shown in Fig. 6 and the light off curves shown in Fig. S5.† T_{90} s for CO/THCs/ NO_x were achieved at 207 °C/244 °C/256 °C over Pt/CeO_2 spheres (DG), respectively. The performance improved with the incorporation of 0.1 molar concentration of Zr. Specifically, $\text{Pt}/0.9\text{CeO}_2@0.1\text{ZrO}_2$ (DG) achieved T_{90} s for CO (188 °C), THCs (229 °C), and NO_x (240 °C) at a lower temperature compared to Pt/CeO_2 spheres (DG). Further, $\text{Pt}/0.8\text{CeO}_2@0.2\text{ZrO}_2$ (DG) showed a slightly improved performance compared to $\text{Pt}/0.9\text{CeO}_2@0.1\text{ZrO}_2$ (DG) with T_{90} s achieved at 185 °C, 223 °C, and 234 °C for CO, THCs, and NO_x , respectively. However, a further increase in Zr molar concentration to ≥ 0.3 led to a decrease in the catalytic performance with a shift in T_{90} s to higher temperatures. For instance, the T_{90} s achieved over $\text{Pt}/0.7\text{CeO}_2@0.3\text{ZrO}_2$ (DG) and $\text{Pt}/0.5\text{CeO}_2@0.5\text{ZrO}_2$ (DG) were 206 °C/245 °C/254 °C and 216 °C/255 °C/268 °C for CO/THCs/ NO_x , respectively. The decreased performance of the catalysts with Zr loadings ≥ 0.3 can be attributed to sintering of Pt particles on crystallized ZrO_2 . Furthermore, the activity of 1.8 wt% $\text{Pt}/\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ (DG) was compared to 1.8 wt% $\text{Pt}/0.9\text{CeO}_2@0.1\text{ZrO}_2$ (DG) (Fig. S6a†). The results indicate that $\text{Pt}/0.9\text{CeO}_2@0.1\text{ZrO}_2$ (DG) outperformed $\text{Pt}/\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ (DG), with the latter achieving T_{90} s of CO/THCs/ NO_x at 205 °C/248 °C/260 °C, respectively.

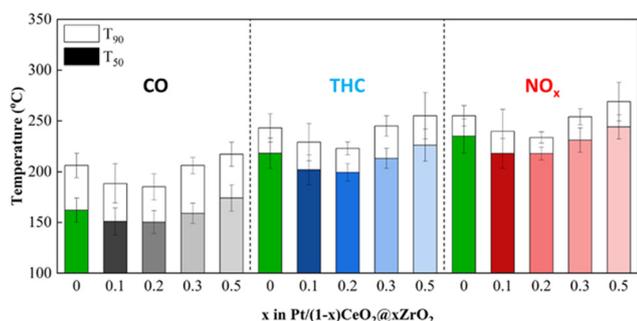


Fig. 6 Comparison of $T_{50,90}$ s of CO, THCs and NO_x over DG 1.8 wt% $\text{Pt}/(1-x)\text{CeO}_2@x\text{ZrO}_2$ ($x = 0, 0.1, 0.2, 0.3, 0.5$) catalysts; each bar represents the average $T_{50,90}$ s of three different batches of the catalyst and the error bars represent the standard deviation of the $T_{50,90}$ s.

The oxygen storage/release properties of the catalyst are crucial in near stoichiometric TWC reactions. Therefore, the OSCC and ORR of $\text{Pt}/(1-x)\text{CeO}_2@x\text{ZrO}_2$ (DG) were measured and correlated with the catalytic performance results (Fig. 7 and S7†). The Pt/CeO_2 sphere had an OSCC and ORR of 155 $\mu\text{mol g}^{-1}$ and 4.7 $\mu\text{mol g}^{-1} \text{s}^{-1}$, respectively. The OSCC and ORR were improved when a small amount of ZrO_2 ($x = 0.1, 0.2$) was deposited on CeO_2 spheres. Specifically, $\text{Pt}/0.9\text{CeO}_2@0.1\text{ZrO}_2$ and $\text{Pt}/0.8\text{CeO}_2@0.2\text{ZrO}_2$ had a greater OSCC (259 and 246 $\mu\text{mol g}^{-1}$, respectively) and ORR (5.2 and 5.1 $\mu\text{mol g}^{-1} \text{s}^{-1}$, respectively) compared to Pt/CeO_2 spheres. However, further addition of Zr (molar concentrations >0.2) decreased the OSCC and ORR. Specifically, the OSCC decreased to 211 and 185 $\mu\text{mol g}^{-1}$ and the ORR decreased to 4.6 and 4.1 $\mu\text{mol g}^{-1} \text{s}^{-1}$ for Zr molar concentrations of 0.3 and 0.5, respectively. Fig. 7 shows that an increase in OSCC and ORR was accompanied by a decrease in T_{50} s and *vice versa*, implying that optimization of the OSCC and ORR of $\text{Pt}/(1-x)\text{CeO}_2@x\text{ZrO}_2$ (DG) by varying the Zr molar concentrations can tune the TWC performance. The ORR of bare supports was measured at three different temperatures (150, 350, and 550 °C). $0.7\text{CeO}_2@0.3\text{ZrO}_2$ showed an enhanced ORR compared to CeO_2 spheres at 150 °C and a similar ORR compared to CeO_2 spheres at 350 and 550 °C (Fig. S8†). Moreover, $0.7\text{CeO}_2@0.3\text{ZrO}_2$ and the $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ solid solution showed a similar ORR at 150 °C, while $0.7\text{CeO}_2@0.3\text{ZrO}_2$ showed a greater ORR than the $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ solid solution at 350 and 550 °C.

The hydrothermal stability of $\text{Pt}/(1-x)\text{CeO}_2@x\text{ZrO}_2$ was assessed after redox HTA was conducted, followed by a TWC performance evaluation. The evaluation results of $\text{Pt}/(1-x)\text{CeO}_2@x\text{ZrO}_2$ (HTA) catalysts are summarized in Fig. 8 and Fig. S9.† All catalysts showed higher $T_{50,90}$ s compared to their DG states (Fig. 6), suggesting that the catalysts deactivate after redox HTA. For example, the Pt/CeO_2 sphere (HTA) reached T_{90} s for CO/THCs/ NO_x at 222 °C/252 °C/258 °C, which are 15 °C/8 °C/3 °C higher than the T_{90} s achieved over Pt/CeO_2 sphere (DG), respectively. Deposition of the Zr shell with a Zr molar concentration <0.2 alleviated the

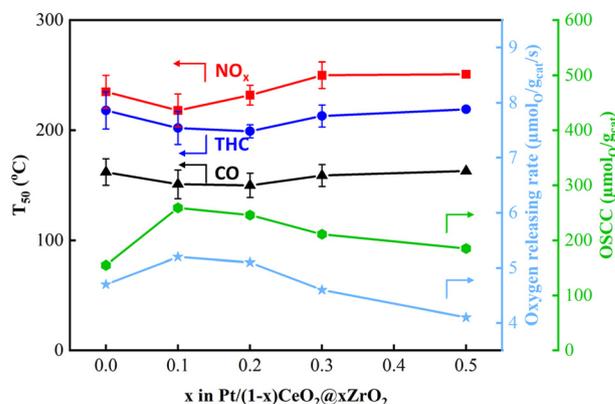


Fig. 7 T_{50} s of CO, THCs, NO_x (left) and OSCC and ORR (right) of 1.8 wt% $\text{Pt}/(1-x)\text{CeO}_2@x\text{ZrO}_2$ (DG) catalysts.



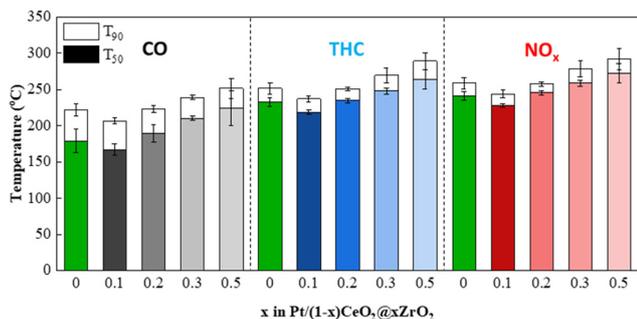


Fig. 8 Comparison of $T_{50,90}$ s of CO, THCs and NO_x for 1.8 wt% Pt/(1 - x)CeO₂@xZrO₂ (HTA) ($x = 0, 0.1, 0.2, 0.3, 0.5$) catalysts; each bar represents the average $T_{50,90}$ s of the three different batches of the catalyst and the error bars represent the standard deviation of the $T_{50,90}$ s.

deactivation caused by redox HTA and improved the catalytic performance compared to the Pt/CeO₂ sphere (HTA). For instance, Pt/0.9CeO₂@0.1ZrO₂ (HTA) achieved lower T_{90} s for CO (207 °C), THCs (237 °C), and NO_x (244 °C) compared to Pt/CeO₂ (HTA) with T_{90} s for CO/THCs/NO_x achieved at 222 °C/252 °C/258 °C, respectively. Moreover, Pt/0.9CeO₂@0.1ZrO₂ (HTA) outperformed Pt/0.8CeO₂@0.2ZrO₂ (HTA) (CO/THCs/NO_x T_{90} s achieved at 223 °C/251 °C/258 °C, respectively). A further increase in Zr molar concentrations to 0.3 and 0.5 led to higher T_{90} s for Pt/0.7CeO₂@0.3ZrO₂ (HTA) (239 °C (CO)/270 °C (THCs)/279 °C (NO_x)) and Pt/0.5CeO₂@0.5ZrO₂ (HTA) (252 °C (CO)/289 °C (THCs)/292 °C (NO_x)). Finally, Pt/0.9CeO₂@0.1ZrO₂ (HTA) outperformed the Pt/Ce_{0.9}Zr_{0.1}O₂ (HTA) (Fig. S6†) solid solution catalyst, with the latter achieving T_{90} s at 220 °C/262 °C/263 °C for CO/THCs/NO_x, respectively. This behavior indicates the advantage of the formation of the (1 - x)CeO₂@xZrO₂ structured support compared to the bare CeO₂ support. TEM images of redox HTA Pt/0.9CeO₂@0.1ZrO₂ (Fig. S10†) showed mild sintering of the spherical support, while no large Pt nanoparticles were identified, which is consistent with the CO-DRIFTS results (Fig. 4). Pt/CeO₂ and Pt/0.9CeO₂@0.1ZrO₂ showed the lowest ΔT_{50} s (= $T_{50,\text{HTA}} - T_{50,\text{DG}}$) (Fig. S11†), suggesting the least deactivation after redox HTA compared to the rest of the studied catalysts. The ΔT_{50} s increased when the Zr molar concentration increased to values ≥ 0.2 , indicating that a thick ZrO₂ coating layer does not favor stability.

4. Conclusions

A simulated S-GDI gas mixture was used for the TWC evaluation of a series of Pt/(1 - x)CeO₂@xZrO₂ catalysts. Pt/CeO₂ spheres (DG) achieved T_{90} s at 207, 244, and 256 °C for CO, THCs, and NO_x, respectively. However, deactivation was observed after HTA with the T_{90} s of the Pt/CeO₂ sphere (HTA) increased to 222, 252, and 258 °C for CO, THCs, and NO_x, respectively. With the incorporation of 0.1 molar concentration of Zr, Pt/0.9CeO₂@0.1ZrO₂ showed the most promising performance

considering both DG and HTA evaluation results by achieving the lowest T_{90} s for CO, THCs, and NO_x at 207, 237 and 244 °C (HTA), respectively, compared to all studied Pt/(1 - x)CeO₂@xZrO₂ catalysts. Tuning the Zr molar concentration and thus the Ce:Zr molar ratio of the Pt/(1 - x)CeO₂@xZrO₂ TWCs affected their low temperature catalytic activity by altering their OSCC and ORR. Specifically, improved OSCC (259 $\mu\text{mol g}^{-1}$) and ORR (5.2 $\mu\text{mol g}^{-1} \text{s}^{-1}$) values were observed over Pt/0.9CeO₂@0.1ZrO₂ (DG), while increasing the Zr molar concentration further led to a decrease in OSCC and ORR. Furthermore, sintering of Pt can be minimized (average Pt particle size of 6.8 nm) over Pt/0.9CeO₂@0.1ZrO₂ compared to an excess amount of zirconium ($x > 0.2$), which contains thick ZrO₂ shell that interacts weakly with Pt. Overall, this work highlights the potential of Pt-only catalysts supported on (1 - x)CeO₂@xZrO₂ supports as TWCs and reveals that an improved TWC performance can be achieved by incorporating moderate amounts of zirconium (Zr molar concentration = 0.1).

Data availability

The data supporting this article have been included as part of the ESI.† Any additional data are available from the corresponding author upon request.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partially supported by start-up funding from the Department of Chemical and Biological Engineering, University at Buffalo (UB), The State University of New York (SUNY). A portion of this research was sponsored by the U. S. Department of Energy's Vehicle Technology Office, with particular thanks to Gurpreet Singh, Siddiq Khan, and Nicholas Hansford of the Offroad, Rail, Marine and Aviation (ORMA). Additionally, the FEI Talos F200X STEM was provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program and the Nuclear Science User Facilities.

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