Thermally Stable RuO_x-CeO₂ Nanofiber Catalysts for Low-Temperature CO Oxidation

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ABSTRACT

With the ever-growing concerns for sustainable energy production and clean air, developing highly efficient catalysts to eliminate exhaust emission pollutants is of vital importance. In this work, we report a class of thermally stable RuO_x-CeO₂ nanofiber catalysts derived from a facile one-pot electrospinning method. Ru-CeO₂ nanofiber catalysts exhibit outstanding low-temperature activity (~ 90% conversion of CO below 150 °C) and long-term durability. The as-prepared Ru-CeO₂ nanofiber catalysts show high BET surface area (> 110 m²/g), demonstrating the effectiveness of electrospinning for fabricating high-surface-area catalysts. Ru-CeO₂ nanofiber catalysts have a hollow interior and porous exterior structure, particularly at the Ru-CeO₂ nanofiber interfaces, providing plentiful accessible CO and oxygen adsorption sites which are beneficial for CO catalytic oxidation. H₂ temperature-programmed reduction (H₂-TPR) was applied to probe the

reducibility of the as-synthesized catalysts. The reduced Ru-CeO₂ nanofiber catalysts exhibited hydrogen consumption near room temperature. The catalysts were further characterized by SEM, EDX and TEM to explore the relationship between microstructure and the extraordinary low-temperature reducibility, as well as the CO oxidation activity. In addition, XPS, *in situ* CO-DRIFTS, and DFT calculation were employed to investigate the chemical states of the active surface species and identify the gas adsorption and reaction sites.

Keywords: electrospinning, ruthenium-ceria nanofiber, reduction treatment, sinter-resistant catalyst, low-temperature CO oxidation, DFT calculation

INTRODUCTION

Development of highly efficient catalysts with improved low-temperature activity to meet the increasingly stringent exhaust emissions standards has been a constantly pursued aim.¹ Most common catalysts in industrial applications are supported metal catalysts, which involve noble metal species as the active components and metal oxides as the support. Ceria (CeO₂) and related materials have become one of the most sought-after supports, promoters or catalysts in automotive exhaust clean-up due to remarkable redox properties and oxygen storage-release capacity.²⁻⁴ For instance, Zhang et al. designed Fe₂O₃-CeO₂@Al₂O₃ nanoarrays catalysts on Al-Mesh and demonstrated its SO₂ tolerance, as well as improved catalytic activity toward low-temperature selective catalytic reduction (SCR) of NO_x with NH₃.⁵ In particular, CeO₂ of nanoscale tailored morphologies such as nanorods, nanocubes, nanotubes, and nanospheres etc. endows the CeO₂-based catalysts with further enhanced activity and selectivity compared to CeO₂ of non-defined morphologies.⁶⁻⁸ For example, the Yan group's hydrothermal methodology for production of shape-controlled nanoceria demonstrated that CeO₂ nanorods with exposed {100}/{110} surface

planes exhibited higher oxygen storage capacity (OSC) and were more reactive than {100} planedominated nanocubes and {111} plane-dominated nanoctahedra.⁹ Zhang et al comparatively examined the morphology-dependent activity of Ni/CeO₂ catalysts toward carbon dioxide reforming of methane, and revealed that Ni species deposited on CeO₂ nanorods, exhibited superior catalytic activity and coke resistance.¹⁰ They attributed the superiority of Ni/CeO₂ nanorods catalyst to the strong metal-support interaction effect and abundant oxygen vacancies. However, the thermal stability of nanoshaped particles is limited. Above 500-600 °C nanoshaped CeO₂ will typically transform into thermally stable octahedral shape with eight "inactive" {111} terminated surfaces.^{11, 12} Alternatively, CeO₂ nanofibers based catalysts have emerged as a novel class of high-performance catalytic materials due to many intriguing advantages, i.e. high surface area and porosity, good chemical stability and sintering resistance, exceptional scale-up flexibility and alignability. For instance, a study of Cu-doped CeO₂ nanofiber catalysts (Cu_{0.1}Ce_{0.9}O_{2-x} nanofibers) revealed the superior catalytic activity compared to counterpart nanoshaped particles for preferential oxidation of CO (CO-PROX).¹³ Moreno et al. synthesized a one-step electrospun Au/CeO₂ nanofiber catalyst with the Au species grown directly during the electrospinning process and a two-step Au/CeO₂ nanofiber catalyst with synthesis of CeO₂ nanofibers followed by deposition of gold nanoparticles.¹⁴ In a CO-PROX comparison study between the one and two step synthesis for Au/CeO₂ nanofiber catalysts, the conversion, activity, selectivity and thermal stability of the one step synthesized Au/CeO₂ nanofiber catalysts clearly outperformed the two step synthesized CeO₂ nanofiber supported Au catalysts.¹⁴ The increased performance of the one step synthesized Au/CeO₂ nanofiber catalyst was attributed to the stronger gold-CeO₂ interaction that helped minimize gold nanoparticles sintering.¹⁴

Significant research efforts to develop more value-added Ru-based catalysts are due, in part, to the low cost of Ru compared to other platinum group elements such as Pt, Pd and Rh. Recently, ruthenium containing catalysts have attracted considerable interest for many reactions including ammonia synthesis, CO2 hydrogenation, hydrocarbon reforming, water splitting and CO oxidation.^{15-18,} Particularly, Ru-based catalysts demonstrated extraordinary activity for low temperature CO oxidation.¹⁹⁻²¹ For instance, Scirè and co-workers have reported the synthesis of Ru-Pd bimetallic catalysts supported on CeO2-MnOx oxides, which exhibit excellent lowtemperature catalytic activity for CO preferential oxidation.²² Chen et al. developed a Ru-Co₃O₄ nanocomposite catalyst which can completely convert CO to CO₂ at temperature as low as 75 °C.²³ Li et al. reported that a 5.0 wt% Ru catalyst supported on CeO₂ nanorods exhibited ~9% CO conversion at near ambient temperature.^{24, 25} Besides, Chen et al. performed density functional theory (DFT) computations over single atom Ru catalysts that anchored on CeO₂(111), TiO₂(110) and Al₂O₃(001) surfaces, of which Ru₁/CeO₂(111) was identified as the most stable and active catalysts for CO oxidation.²⁶ Nevertheless, studies elucidating the mechanism of CO oxidation activity over Ru catalysts have long been inconclusive.²⁷

In this work, we employ DFT calculations to investigate CO oxidation over Ru doped CeO₂(111) surfaces, which provides mechanistic understanding and theoretical basis for the design of highly active Ru-CeO₂ catalyst. We also report a simple strategy to fabricate a novel Ru-CeO₂ nanofibers catalyst (1RuO_x-CeO₂NF) with 1 wt% ruthenium loading, as well as pristine CeO₂ nanofibers (CeO₂NF) via an electrospinning technique (Figure 1) followed by a calcination process. This one-pot electrospinning process without an aqueous precipitation-impregnation catalyst loading step presents a facile route toward highly active and cost-effective catalyst fabrication and can be extended towards scalable nano-manufacturing. Further reduction treatment of the as

calcined 1RuO_x-CeO₂NF produces the reduced Ru-CeO₂ nanofibers (1Ru-CeO₂NF) catalyst. Reduction treatment to produce 1Ru-CeO₂NF improves low-temperature conversion efficiency and long-term durability for CO oxidation due to promoted Ru diffusion into the CeO₂ lattice. The structure-activity relationship and the active sites for the Ru-CeO₂ nanofiber catalysts in CO oxidation reaction are also discussed.

COMPUTATIONAL METHODS

Spin-polarized calculations were performed in the Dmol³ package based on density functional theory.²⁸ Perdew-Burke-Ernzerhof (PBE) function within the generalized gradient approximation (GGA) was adopted to describe the electron exchange-correlation interaction.²⁹ Double numerical plus polarization (DNP) was selected as the atomic orbital basis set, with global orbital cut-off radius of 5.0 Å and smearing of 0.005 Ha to ensure high computational accuracy. The Monkhorst-Pack k-point mesh of 3×3×1 is set for all super-cell geometry optimizations and electronic structure calculations.³⁰ A 2×2 supercell with 17 Ce and 34 O atoms was established for the CeO₂ (111) surface with a vacuum of 15 Å to conduct the whole calculations. The calculated lattice constant is 3.32 Å, in agreement with previous reports.³⁰ Figure 2a portrays the optimized geometric structures of pure and Ru-doped CeO₂ (111) surfaces, in which the central Ce atom is substituted by a Ru atom to form the Ru-doped counterpart. The adsorption energy (E_{ad}) is introduced to estimate the adsorption performance of analyzed surface upon targeted gas molecules, expressed as: $E_{ad} = E_{surf/gas} - E_{surf} - E_{gas}$, in which $E_{surf/gas}$, E_{surf} and E_{gas} are the energies of gas adsorbed surface, isolated surface and isolated gas molecule, respectively. In addition, Hirshfeld method is considered to analyze the atomic charges in adsorption, based on which the positive value means electron-donating behavior of related analytes.

EXPERIMENTAL SECTION

Materials. Cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99.5%) was purchased from Acros Organics. Ruthenium (III) Nitrosylnitrate (Ru(NO)(NO₃)₃, Ru 31.3% min.), N, N-dimethylformamide (DMF, 99.7+%) and Polyvinylpyrrolidone (PVP, Mw = 1,300,000) were supplied by Alfa Aesar. Ruthenium (IV) oxide powder was purchased from Alfa Aesar as well. All the chemicals were used as received without further purification.

Synthesis of Ru/CeO₂NF and pure CeO₂NF. In a typical procedure for the targeted 1 wt% Ru, the precursor/polymer solution was prepared by dissolving 2.1711 g of Ce(NO₃)₃·6H₂O and 0.0273 g of Ru(NO)(NO₃)₃ in 50 mL DMF and kept magnetic stirring at room temperature for 30 min. 6.5175 g PVP was then added to the metal salt solution and stirred for 12 h until the PVP was fully dissolved. $[Ce(NO_3)_3 + Ru(NO)(NO_3)_3]/PVP$ nanofibers were prepared using the Innovenso Nanospinner 24 Multinozzle Electrospinning System. A 20-mL plastic BD syringe was used to load the precursor/polymer solution while the flow rate was controlled by a precision digital syringe pump. The solution was transported from the syringe to a syringe needle connected with a high voltage power supply. The sample collector used was a grounded rotating drum covered by nonstick aluminum foil. The schematic diagram of the setup is shown in Figure 1. The processing parameters were set as follows: applied voltage (25 kV), flow rate (2.0 mL/h) and tip-to-collector distance (15 cm). After electrospinning, the precursor fibers were dried at 60 °C in a vacuum drying oven for 24 h to evaporate the remaining solvent. 1RuOx-CeO2NF catalysts ("1" denotes 1 wt%, calculated based on $[Ru/(Ru + CeO_2)]_{wt} \times 100\%)$ were obtained by calcining the [Ce(NO₃)₃ + Ru(NO)(NO₃)₃]/PVP precursor fibers in a box furnace under air at 500 °C for 3 h with the heating rate of 1°C/min. After that, a portion of the 1RuO_x-CeO₂NF samples underwent thermal reduction treatment in a tube furnace with a gas flow of 5 vol.% H₂/95 vol.% Ar (150 mL/min) at 300 °C for 5 h to obtain the 1Ru-CeO₂NF catalysts. To prepare pure CeO₂NF, the electrospinning process followed the same procedure using Ce(NO₃)₃/PVP precursor/polymer solution without addition of Ru(NO)(NO₃)₃. In order to compare the effectiveness of the electrospinning technique with the conventional strategy for catalysts making, 1Ru/CeO₂NP catalyst was prepared by depositing 1wt% Ru onto CeO₂ nanoparticles following the precipitation-deposition method, and the details are given in Supporting Information.

Characterization. X-ray diffraction (XRD) was performed on a Philips X'Pert MPD diffractometer with Cu K α radiation (λ =1.5405 Å) operating at 45 kV and 40 mA. Rietveld refinement analysis of XRD patterns was carried out using the Bruker-Topas software. Raman spectra were recorded on a Horiba LabRam HR800 microscope using a 532 nm laser and a grating of 1800 grooves/mm. The X-ray photoelectron spectroscopy (XPS) was measured with a Kratos Axis DLD spectrometer using monochromatic Al K α radiation (hv = 1486.6 eV) under UHV condition (< 8x10⁻¹⁰ Torr). Prior to the data analysis, all spectra were calibrated by referencing the binding energy of C 1s peak at 284.8 eV. Scanning electron microscopy (SEM) images were collected using a Thermo Scientific Apreo FE-SEM. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HAADF-STEM) and STEM-EDS mapping images were collected on a FEI Tecnai F20 microscope (equipped with an EDAX energy dispersive X-ray system) at an accelerating voltage of 200 kV.

H₂-TPR was performed on a Micromeritics AutoChem II 2920 chemisorption analyzer equipped with a thermal conductivity detector (TCD). *Ca.* 90 mg of catalyst, a temperature range of 30 to 900 °C with a heating rate of 10 °C/min, and a flow rate of 50 mL/min of 10 vol.% H₂/Ar were used for the H₂-TPR measurements. Single-point Brunauer–Emmett–Teller (BET) surface area for catalysts was determined by N₂ adsorption/desorption at ~77 K on the same instrument.

In situ diffuse reflectance infrared spectroscopy (DRIFTS) measurements were performed on a Bruker Vertex 70 FTIR spectrometer equipped with a Harrick DRIFTS cell and measured using a room temperature DLaTGS detector. Prior to each experiment, the catalysts were pretreated inside the cell in UHP N₂ gas environment with a flow rate of 30 mL/min at 200 °C for 30 min to remove the moisture (heating rate: 10 °C/min). After cooling to 35 °C, the background spectrum was collected at the same flow (30 mL/min UHP N₂). The feeding gas was then switched to 30 mL/min 5 vol.% CO/95 vol.% Ar mixture and kept flowing up to 40 min, after which the flow was switched back to 30 mL/min UHP N₂ gas for another 40 min. During this time, spectra were acquired every 4 min using 64 scans at 4 cm⁻¹.

Themogravimetric analysis (TGA) was performed using a Perkin Elmer STA 8000 thermal analyzer. Samples of *ca*. 30 mg were heated from 25 °C to 900 °C at a heating rate of 10 °C/min in an UHP N₂ flow.

Catalytic activity test. Catalytic activity toward CO oxidation was evaluated using a fixed bed plug flow reactor system, loaded with *ca*. 50 mg of the catalyst packed in between quartz wool. The catalyst was not pretreated before the catalytic activity test. The reaction gas mixture, 1 vol.% CO, 20 vol.% O_2 balanced with helium, was introduced to the catalyst

at a flow rate of 38 mL/min corresponding to a weight hour space velocity WHSV of 46,000 mL·h⁻¹ \cdot g_{cat}⁻¹. The gaseous composition in the reactor effluent was analyzed using an online gas chromatograph (SRI multiple gas analyzer GC) equipped with a TCD detector. CO conversion rate at each reaction temperature was calculated as follows

$$CO \text{ conversion}(\%) = \frac{[CO]_{inlet} - [CO]_{outlet}}{[CO]_{inlet}} \times 100\%$$

Time-on-stream studies for CO conversion were conducted in the same conditions maintained at a constant reaction temperature of 110 °C continuously for 48 h.

RESULTS AND DISCUSSION

DFT calculations were performed to obtain rational guidance for design of a highly effective CO oxidation catalyst. The whole process for CO oxidation over Ru-CeO₂ (111) surface is depicted in Figure 2b. The basis for applying CeO₂ (111) surface as the computational model is formed by the highest stability of the CeO₂ (111) termination at elevated temperature, which is also substantiated by HRTEM. In Figure S1, the adsorption energy (E_{ad}) of O₂ molecule on the Ru-CeO₂(111) surface are calculated. The low E_{ad} values of -0.01 eV, -0.03 eV and -0.11 eV at O, Ce and Ru sites indicate a weak O₂ molecule-surface interaction. While E_{ad} of O₂ is even larger over undoped CeO₂(111) surface (0.53 eV for C e site and 0.55 eV for O site). The adsorption of CO molecule by Ce-end position is analyzed due to no binding or weak-binding occurring for the adsorption by O-end position on surface for both Ru-doped CeO₂(111) and undoped CeO₂(111).³⁰, ³¹ After a full optimization, the Ru-top site is the most favorable configuration for CO adsorption on Ru-CeO₂ (111) surface (Figure S1), with the adsorption energy (E_{ad}) of -1.12 eV, which is significantly more negative than those O-top sites with E_{ad} of ~ -0.25 eV. This indicates that CO adsorption on Ru-top site is the most stable structure and it should be identified as the initial state

(IS1) to initiate the CO oxidation on Ru-CeO₂ (111) surface. As presented in Figure 2b, the C-O bond is somewhat activated to 1.15 Å from that of 1.14 Å in gas phase while the Ru-doped substrate suffers slight deformations. The atomic distance of Ru-C is measured to be 1.98 Å, a little shorter than the sum of the covalent radii of Ru and C atoms (2.0 Å).³² These findings indicate the physisorption of CO molecule on the Ru-doped surface, as verified by the adsorption energy of -0.83 eV and negatively charged CO molecule of 0.11 e⁻. To capture a lattice O atom from the Ru-CeO₂ (111) surface, the energy barrier of 0.23 eV should be overcome and then it reaches to the transition state (TS1). In this configuration, one O atom is captured by the CO molecule forming a new C-O bond with the length of 1.90 Å, while the atomic distance of Ru-C is elongated to 2.00 Å. A new CO₂ molecule is then formed and escapes from the surface. In the final state (FS1), the CO₂ molecule becomes a linear structure with the nearest distance to the catalyst surface measured to be 3.79 Å. Thus, it is expected that the formed CO₂ molecule could release from the surface without much energy consumption. The calculated E_{ad} for CO₂ release is calculated to be -0.11 eV, lower than -0.5 eV,³³ which confirms the easy release of the formed CO₂ molecule from the O-defected Ru-CeO₂ (111) substrate. The relative energy between IS1 and FS1 is -1.43 eV, which demonstrates that the CO oxidation over $Ru-CeO_2$ (111) surface is exothermic. This is beneficial for surface interactions in the following processes. To repair the O-vacancy on Ru-CeO2 (111) surface, the interaction with a surrounding O_2 molecule at the vacancy is significant, and in that case there would be an extra O atom standing outside of the surface, which accordingly offers the possibility to conduct another cycle of CO oxidation. The catalyst regeneration process begins with the physisorption of another CO molecule on the O-covered Ru-CeO₂ (111) surface with E_{ad} of 0.67 eV and negatively charged CO of 0.05 e⁻, wherein CO molecule is adsorbed with C-end position and the C-O distance is measured to be 2.02 Å. For striding the TS2 and finally reaching to FS2 with the formation of CO₂ molecules, the extra O on the Ru-CeO₂ (111) surface needs to be removed first, of which the energy barrier is calculated to be only 0.18 eV. The calculated energy barrier for removing the extra O on the Ru-CeO₂ (111) surface to reach the TS2 is only 0.18 eV. From the molecular point of view, the CO₂ molecule is positively charged by 0.02 e⁻, implying that it has little charge effect on the repaired surface. The long molecular distance between the formed CO₂ molecule and the substrate surface (3.64 Å) associated with the small E_{ad} of -0.30 eV confirm that the release of CO₂ molecule from the repaired Ru-CeO₂ (111) substrate is feasible. The density of state distributions of repaired Ru-CeO₂ (111) are essentially overlapped with that of clean Ru-CeO₂ (111), which indicates the stable electronic behavior and its good recyclability for CO oxidation, as seen in Figure S2. Moreover, the Vibrational Spectra analysis shows that all transition states have the single imaginary frequencies, which verifies the reliability of our obtained transition states.

Electrospinning was employed for the design of both pure CeO₂NF and Ru-CeO₂NF catalysts due to simplicity, controllability, scalability and cost effectiveness benefits.³⁴ To start with, Ce(NO₃)₃/PVP and [Ce(NO₃)₃ + Ru(NO)(NO₃)₃]/PVP precursor fibers were electrospun. According to TGA results, there were two weight-loss steps for the electrospun Ce(NO₃)₃/PVP, Figure S3. The first step (< 350 °C) resulting in weight loss of *ca*. 13% corresponds to the decomposition of Ce(NO₃)₃·6H₂O, while the second step from 350 °C to 500 °C is due to the decomposition of PVP based upon TGA curves of pure Ce(NO₃)₃·6H₂O and PVP, Figure S3. Based on the TGA results, the calcination temperature of 500 °C was determined for the complete conversion of polymeric precursor into nanocrystalline phase. The reduced 1Ru-CeO₂NF catalyst was obtained by an additional reduction treatment. To allow for comparison, commercial RuO₂ powder underwent the same calcination and reduction procedures to obtain unsupported RuO₂ and

Ru catalysts. The catalytic activities of electrospun CeO₂NF, 1RuO_x-CeO₂NF, 1Ru-CeO₂NF, as well as commercial RuO₂ and Ru catalysts for CO oxidation are shown in Figure 3a. Catalyst ranking based upon the light off temperature (T_{50}) for CO oxidation is: 1Ru-CeO₂NF ($T_{50} = 78 \text{ °C}$) > 1 RuO_x-CeO₂NF ($T_{50} = 98 \text{ °C}$) > 1 Ru/CeO₂NP ($T_{50} = 112 \text{ °C}$) > RuO₂ ($T_{50} = 179 \text{ °C}$) > Ru (T_{50} = 238 °C) > CeO₂NF (T_{50} = 326 °C). The electrospun Ru-CeO₂NF catalyst demonstrates superior catalytic activity at low temperature, which agrees with the DFT calculations. Compared to the CeO₂NF, RuO₂ and Ru catalysts, the superior catalytic performance of the Ru-CeO₂NF suggests synergy or strong interaction between Ru species and CeO_2NF . Additionally, by comparing with classical 1Ru/CeO₂NP catalyst prepared through the precipitation-deposition method, the 1Ru/CeO₂NF catalyst that obtained by this facile and controllable electrospinning route exhibits more excellent low-temperature CO conversion activity. On-stream catalyst durability for 1Ru-CeO₂NF, 1 RuO_x-CeO₂NF and CeO₂NF was determined with constant temperature (110 °C) CO oxidation. As shown in Figure 3b, the reduced 1Ru-CeO₂NF catalyst demonstrates the best longterm durability, 88.4% initial CO conversion and retains 83.0% conversion (6.1% decrease) after 48 h. The on-stream CO conversion rate for the 1RuO_x-CeO₂NF catalyst decreased from 75.4% to 53.2% (29.4% decrease) over 48 h. No CO conversion was observed for CeO₂NF at 110 °C for 48 h. The on-stream catalyst durability experiments indicate that the reduction treatment of 1RuOx-CeO₂NF to 1Ru-CeO₂NF activates low temperature CO catalytic oxidation activity and promotes the long-term durability, possibly due to the enhanced Ru diffusion into CeO₂ lattice or RuO_x-CeO₂ mixing. As reported previously, the Ru cationic sites are more active for CO oxidation compared to the metallic Ru sites.²⁵

Figure 4a shows the XRD patterns of the electrospun CeO₂NF, 1RuO_x-CeO₂NF, and 1Ru-CeO₂NF catalysts as well as the commercial RuO₂. All nanofiber samples display four major

diffraction peaks at *ca*. 28.6°, 33.0°, 47.5°, and 56.5° which can be indexed to (111), (200), (220), and (311) planes respectively of CeO₂ (JCPDS #34-0394, space group Fm-3m) with a FCC fluorite structure. For 1RuO_x-CeO₂NF or 1Ru-CeO₂NF catalysts, no new diffraction peaks of Ru related phase (RuOx or metallic Ru) were observed, which indicates that all Ru species were completely incorporated into CeO₂ lattice or highly distributed on the CeO₂NF surface. In addition, the absence of Ru species related peaks could also be due to the low loading amount of Ru. The lattice parameters of the nanofiber samples were analyzed based on the Rietveld refinements, and the specific values were presented in Table 1. It is noted that the lattice constant of 1RuO_x-CeO₂NF decreases a small amount from a = 5.4100 Å (for CeO₂NF) to a = 5.4070 Å. The lattice constant shrinkage is attributed to the smaller cation radius of Ru^{4+} (0.62 Å) compared to that of Ce^{4+} (0.97 Å), confirming the incorporation of Ru species into CeO₂ lattice.³⁵ After the reduction treatment, a slight lattice expansion was observed on the 1Ru-CeO₂NF catalyst (a = 5.4082 Å) in comparison with that of the 1RuO_x-CeO₂NF catalyst, which might be due to the reduction of small amount of Ce^{4+} to Ce^{3+} (ionic radii: $Ce^{4+} = 0.97$ Å and $Ce^{3+} = 1.143$ Å).³⁶ This phenomenon was verified by the relative Ce^{3+} concentration in CeO_{2-x} using XPS analysis listed in Table 1, with $Ce^{3+}/(Ce^{3+} +$ Ce^{4+}) ratio rising from 25.7 % to 30.7 %. The other possible reason related to the lattice expansion is the reduction (or partial reduction) of Ru⁶⁺, which also increases the ionic radius. All three electrospun fibrous catalysts show a similar crystallite size, suggesting the excellent thermal stability of electrospun catalysts through the oxidation and reduction treatments. Raman analysis of all catalyst samples were then performed to investigate the elemental coordination environment and crystal defects, Figure 4b. For CeO₂NF, the strongest peak located at 464 cm⁻¹ is attributed to a symmetrical stretching mode (F2g) of the Ce-O8 vibrational unit, while the peak at 598 cm⁻¹ is related to the defect-induced mode (D).^{37, 38} The inset in the Raman spectrum of CeO₂NF shows

an enlarged region from 200 to 400 cm⁻¹, where the peak at 260 cm⁻¹ is assigned to the secondorder transverse acoustic (2TA) vibrational mode.³⁹ The F_{2g} band for both calcined 1RuO_x-CeO₂NF catalyst and reduced 1Ru-CeO₂NF catalysts shifted to a lower wavenumber, 460 cm⁻¹, corroborating Ru diffusion into CeO₂ lattice or the formation of Ru-O-Ce solid solution.⁴⁰ Also, the shift of F_{2g} band to lower wavenumbers coincides with the decreased lattice constant of CeO₂ observed from XRD results.³⁹ The Raman peaks at 240 cm⁻¹ and 395 cm⁻¹ are assigned to the longitudinal stretching mode of the topmost O-Ce layer and the transverse stretching mode of the surface oxygen against the cerium ion, respectively.⁴¹ The additional peaks at 702 cm⁻¹ and 970 cm⁻¹ observed for 1RuO_x-CeO₂NF and 1Ru-CeO₂NF catalysts have been widely detected from Ru/CeO₂ system in literature.^{17, 42} However, those Raman peaks cannot be assigned as either single-phase CeO₂ or RuO₂ (as referred to the CeO₂NF and commercial RuO₂ Raman spectra), but were commonly designated to the Ru–O-Ce bond formed resulted from the interaction between Ru species and CeO₂.^{43, 44}

The chemical states of the surface Ru species were analyzed by XPS. The XPS spectra of both survey scan and high-resolution Ru 3d region for all investigated catalysts are displayed in Figure 5. In the case of 1RuO_x -CeO₂NF catalyst, the deconvolution of the Ru 3d core-level spectrum reveals the existence of four peaks centered at 281.8, 282.5, 286.0, and 286.7 eV that are attributed to Ruⁿ⁺ 3d_{5/2} (4<n<6), Ru⁶⁺ 3d_{5/2}, Ruⁿ⁺ 3d_{3/2} (4<n<6), and Ru⁶⁺ 3d_{3/2}, respectively.⁴⁵ For the reduced 1Ru-CeO₂NF catalyst, the deconvoluted peaks at 282.1 and 286.3 eV in Ru 3d spectrum still reveal the presence of Ruⁿ⁺ (4<n<6) species. New components appear at binding energies of 281.1 and 285.3 eV that corresponded to the Ru⁴⁺ 3d_{5/2} and Ru⁴⁺ 3d_{3/2} spin-orbit coupling in the 1Ru-CeO₂NF catalyst.⁴⁶ Ru 3d spectrum obtained from the commercial RuO₂ sample demonstrates that the Ru species existed solely as Ru⁴⁺. Binding energies locating at 280.3

and 284.5 eV for Ru⁴⁺ 3d_{5/2} and Ru⁴⁺ 3d_{3/2}, respectively, were found for commercial RuO₂.⁴⁷ Two satellite peaks (sat.) of the Ru⁴⁺ 3d spin orbital doublets appear at 282.1 and 286.3 eV. The presence of Ruⁿ⁺(4<n<6) binding energies that are different from the binding energy in both RuO₂ and RuO₃ suggests possible electron transfer from Ru to CeO2 at the interface or the formation of Ru-O-Ce bond.⁴⁸ Relative surface quantification of Ru species over the Ru-CeO₂NF catalysts is listed in Table 1. Relative surface quantification of Ru species combined with CO conversion results tentatively indicates that a Ruⁿ⁺(4<n<6)/Ru⁴⁺-rich surface is more favorable for CO catalytic oxidation at low temperature than a $Ru^{n+}(4 \le n \le 6)/Ru^{6+}$ -rich surface. The O 1s spectra of the XPS spectra of the aforementioned catalysts were also investigated, Figure 5d. The broad peaks in the O 1s spectra of all nanofiber samples can be fitted into three different components, lattice oxygen (O_L), oxygen vacancy (O_V), and surface chemisorbed oxygen or oxygen in hydroxyl groups (O_C). Here we define the surface-active oxygen (Oa) as the sum of Ov and O c ($\boldsymbol{O}_a = \boldsymbol{O}_V + \boldsymbol{O}_C$). The intense peaks at *ca*. 529.2 eV corresponds to the lattice oxygen (O_L). The peak at 531.1 eV is attributed to the oxygen vacancy site (O_V). The weak peaks at ca. 534.1 eV are chemisorbed oxygen or -OH groups at a surface defect or assigned to the adsorbed H₂O.⁴⁹⁻⁵¹ The peak areas of the latter two adsorbed oxygen components (O_a) and the primary lattice oxygen (O_L) are integrated to estimate the relative content of the surface active oxygen, and the results of O_a/(O_a+O_L) are listed in Table 1. Literature indicates that oxygen activation on CeO₂ surface can facilitate the CO oxidation.^{52, 53} Compared to the calcined 1RuO_x-CeO₂NF catalyst (20.6%), the reduced 1Ru-CeO₂NF catalyst (24.0%) had more activated surface oxygen which accounts for the improved catalytic performance. The O 1s spectrum for commercial RuO₂ can also be deconvoluted into three components, with the first peak at ca. 529.0 eV originating from Ru-O-

Ru species, the second peak at *ca*. 530.0 eV is due to Ru-O-H species and the last peak at *ca*. 531.2 eV is ascribed to Ru-H₂O.^{54, 55}

H₂-TPR (Figure 6a) was applied to probe the reduction temperature and hydrogen consumption of CeO₂NF as well as the corresponding catalysts. For CeO₂NF, the major reduction peak at 463 °C is attributed to the reduction of surface Ce⁴⁺, while the high temperature reduction peak at 738 °C corresponds to the bulk reduction of Ce⁴⁺. The H₂-TPR profile of the 1RuO_x-CeO₂NF catalyst exhibits a low temperature peak at 92 °C, which is associated with the reduction of RuO_x species (Ru^{6+} and $Ru^{n+} \rightarrow Ru^0$ in this case).^{25, 56} The peak related to the reduction of surface Ce⁴⁺ species moved to lower temperature at 294 °C. Interestingly, the 1Ru-CeO₂NF catalyst still exhibits a reduction peak at 70 °C, albeit with a decreased intensity. The 1Ru-CeO₂NF low temperature reduction peak is associated to the strong Ru-CeO₂ interaction or the formed Ru-O-Ce bond.^{48, 56} The much lower reduction temperature for reduction of surface Ce⁴⁺, 264 °C for1Ru-CeO₂NF sample compared to 294 °C for 1RuO_x-CeO₂NF, indicates a stronger interaction of Ru with CeO₂ causing Ce-O bond relaxation,^{24, 35} which can be induced by the reduction treatment. Additionally, the commercial RuO₂ only exhibited one broad reduction peak at 111 °C, which was due to the reaction: $RuO_2 + 2H_2 \rightarrow Ru^0 + 2H_2O^{.57}$ The reducibility of the catalysts was further evaluated by calculating the H₂ consumption (Figure 6b). Herein, H₂ consumption values were normalized based on the 1 wt.% Ru active component and 99 wt.% CeO₂ support. Both the surface (low temperature up to 300 °C) and total H₂ consumption (up to 900 °C) values of the fibrous Ru-CeO₂NF catalysts are much higher than the scaled sum of CeO₂NF and commercial RuO₂. The increased H₂ consumption indicates promotion of reduction due to the synergism/strong metal-support interaction between Ru species and CeO₂.

The BET surface area (Table 1) of CeO₂NF, 1RuO_x-CeO₂NF, 1Ru-CeO₂NF catalysts and commercial RuO₂ were measured to be 116 m²/g, 111 m²/g, 117 m²/g and 20 m²/g (error ranges: $\pm 6 \text{ m}^2/\text{g}$) respectively, demonstrating that the electrospinning technique is an effective method for high-surface-area catalysts fabrication, that inclusion of Ru does not change the specific surface area, and that the NF samples are resistant to sintering during postprocessing. Figure 7b and 7c depict the typical low- and high-magnification SEM images of Ce(NO₃)₃/PVP precursor fibers, of which smooth surfaces and network structure with an average diameter of *ca*. 200 nm are clearly visible. After calcination, the fiber-like morphology was retained, but the average diameter of CeO₂NF decreased to ca. 100 nm (Figure 7d), which is due to the removal of PVP. Figure 7e and f present the SEM images of the electrospun $[Ce(NO_3)_3 + Ru(NO)(NO_3)_3]/PVP$ precursor fibers with a diameter of 100-150 nm, a uniform fibrous morphology, and a glossy surface. After calcination at 500 °C and reduction treatment at 300 °C, the 1Ru-CeO2NF catalyst still maintains a fibrous framework (Figure 7g), but turns into a crimped morphology with an average diameter ca. 100 nm. As shown in Figure 7h and i, a portion of the 1Ru-CeO₂NF catalyst shows an interconnected nanoparticle-chain comprised of a porous and rough surface structure with a larger diameter measured to be ca. 200 nm. The porous microstructure can provide accessible adsorption sites and may help explain the exceptional low temperature CO oxidation performance of the 1Ru-CeO₂NF catalyst.⁵⁸

TEM analysis (Figure 8a-c), in agreement with SEM results, demonstrates that electrospun CeO₂NF, $1RuO_x$ -CeO₂NF and 1Ru-CeO₂NF all exhibit fiber-like nanostructures with the diameters of *ca*. 92 nm, 108 nm and 133 nm, respectively. Small interconnected nanoclusters with a random arrangement are found on the outer wall of 1Ru-CeO₂NF catalysts, in Figure 8d. The HRTEM image (Figure 8e) reveals a lattice spacing of 0.31 nm that corresponds to the {111}

surface termination of CeO₂.⁵⁹ No apparent Ru nanoparticles/clusters are visible on the surface of the 1Ru-CeO₂NF catalyst, indicating that the Ru species are well-dispersed or incorporated into the CeO₂ lattice. STEM-EDS mapping in Figure 8f confirms the uniform distribution of Ru element in this 1Ru-CeO2NF catalyst, confirming the feasibility of preparing highly dispersed fiber-type catalysts by this facile electrospinning method. A hollow structure was found in the middle of an isolated 1Ru-CeO₂NF fiber during a STEM-EDS line scan, Figure 8g.

In situ DRIFTS was performed to provide the insights into CO interaction with the asdiscussed fiber catalysts, and further elucidate the active surface species. The catalysts were exposed to a flow of 5 vol.% CO balanced with Ar for 40 min until surface adsorption sites were near fully covered by CO molecules. Due to CO flow, gas-phase CO bands at *ca*. 2118 and 2173 cm⁻¹ were detected for all the samples (Figure 9 a-d). Following 40 minutes of CO flow the samples were purged with UHP N₂ flow for 40 minutes. Nitrogen flow with the catalyst slightly above room temperature (35 °C) removed gas phase CO from the system and removed any physisorbed CO species, leaving only chemisorbed CO on the surface of the catalyst. CO-DRIFTS data were collected continuously every 4 min through the whole process. Figure 9b presents the DRIFTS spectrum of CO chemisorption on 1RuO_x-CeO₂NF catalyst at 308 K (35 °C). A strong band found at ca. 2054 cm⁻¹ associated with the 2118 cm⁻¹ band is attributed to multicarbonyl adsorbed on oxidized Ru sites as [Ruⁿ⁺-(CO)_x].⁶⁰ In contrast to the 1RuO_x-CeO₂NF catalyst, CO-DRIFTS of the reduced 1Ru-CeO₂NF catalyst also exhibits the multicarbonyl species adsorbed on "oxidized" Ru sites at 2044 cm⁻¹ and 2116 cm⁻¹. The reduction treatment results in a slightly red shift of the 2054 cm⁻¹ band to 2044 cm⁻¹, consistent with the lowered oxidation states of Ru ($n+/6+\rightarrow n+/4+$) from the XPS results (Figure 5b). While the 2116 cm⁻¹ and 2118 cm⁻¹ bands do occur at the same position as a CO band, they are chemisorbed species as they persist through

N₂ flow at elevated temperature. Both 1RuO_x-CeO₂NF and 1Ru-CeO₂NF catalysts exhibit an absorption band at ~1975 cm⁻¹ or 1977 cm⁻¹. Panagiotopoulou et al. studied CO adsorption over Ru/TiO₂ catalysts and identified the 1975 cm⁻¹ band as adsorbed CO species on Ru sites at the metal-support interface.⁶¹ Chen et al. used First-Principles calculations to study CO adsorption on Ru-doped CeO₂(111) surface and assigned the vibrational frequency 1980 cm⁻¹ as the linearly bonded CO on Ru sites at the Ru-CeO₂ interface.³⁰ So far, agreement has not been reached at this vibrational frequency and CO-DRIFTS of Ru-CeO2 system was seldom reported before. The band at 1975/1977 cm⁻¹ is assigned to linear CO adsorption on Ru species at the Ru-CeO₂ interface. After reduction treatment, a new band emerges at 2017 cm⁻¹ for the 1Ru-CeO₂NF catalyst. The 2017 cm⁻¹ absorption feature is either CO linearly adsorbed at oxidized Ru sites as [Ruⁿ⁺-CO] or CO adsorbed on oxygen vacancies.⁶² No CO chemisorption on CeO₂NF and commercial RuO₂ was detected. Lack of CO adsorption on the bare support or commercial RuO₂ provides indirect evidence that the interfacial sites between Ru and CeO₂NF correspond to the CO adsorption, due to a strong interfacial Ru-CeO₂ interaction (charge transfer or formation of Ru-O-Ce bond) or the incorporation of Ru into CeO₂ lattice by electrospinning.

CONCLUSION

In summary, CO oxidation over Ru-CeO₂(111) surface was demonstrated to be an exothermic process from DFT calculation results. A facile one-pot electrospinning approach was developed to fabricate fibrous CeO₂ and Ru-CeO₂ catalysts. With relative low Ru loading content of 1 wt%, the electrospun Ru-CeO₂NF catalysts exhibited outstanding catalytic activity toward CO oxidation with improved thermal aging resistance. The reduction treatment generated more Ruⁿ⁺ (4<n<6) sites and surface active oxygen, which further enhanced low temperature CO conversion performance and long-term durability. The synergism/strong metal-support interaction between

Ru species and CeO₂ is responsible for the enhanced reactivity of the electrospun Ru-CeO₂NF catalyst. The unique hollow interior and porous exterior structure improved the catalytically active surface site availability for CO molecules which is favorable for catalytic CO Oxidation. The effectiveness of applying electrospinning strategy for developing the highly dispersed and efficient Ru-CeO₂ catalysts was demonstrated as well.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/xxx.

Optimized Ru-CeO₂(111) Cartesian Coordinates in Angstroms; DOS of pure Ru-CeO₂(111) and repaired Ru-CeO₂(111); Adsorption configurations for Ru-CeO₂ (111)/CO system, Ru-CeO₂ (111)/O₂ system, CeO₂ (111)/CO system and CeO₂ (111)/ O₂ system; TGA curves of Ce(NO₃)₃·6H₂O, PVP (M_w = 1,300,000) and electrospun Ce(NO₃)₃/PVP precursor fibers (PDF)

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Notes

The authors have no conflict interest to declare.

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Figure 1. Schematic illustration of one-pot electrospinning synthesis of Ru-CeO₂ nanofiber

catalysts followed by a calcination and reduction treatment.



Figure 2. (a) Geometric structure of pristine CeO₂ (111) surface and Ru-CeO₂ (111) surface and (b) CO oxidation on Ru-CeO₂ (111) surface, the unit of distance is in Å.



Figure 3. (a) CO conversion over RuO₂, Ru, 1Ru/CeO₂NP, 1RuO_x-CeO₂NF, 1Ru-CeO₂NF and CeO₂NF as a function of reaction temperature and (b) Long-term catalytic stability evaluation at 110 °C for 1RuO_x-CeO₂NF, 1Ru-CeO₂NF and CeO₂NF. Reaction conditions: 1 vol.% CO/20 vol.% O₂/He balanced, WHSV = 46, 000 mL·h⁻¹ ·g_{cat}⁻¹.



Figure 4. (a) XRD patterns and (b) Raman spectra of RuO₂, 1RuO_x-CeO₂NF, 1Ru-CeO₂NF and CeO₂NF.



Figure 5. (a) XPS survey spectra, (b) XPS Ru 3d region, (c) XPS Ce 3d region and (d) XPS O 1s region of RuO₂, 1RuO_x-CeO₂NF, 1Ru-CeO₂NF and CeO₂NF. (All curves were fitted based on a Shirley-type background.)



Figure 6. (a) H₂-TPR profiles and (b) Quantitative analysis of H₂ consumption based on H₂-TPR results of RuO₂, $1RuO_x$ -CeO₂NF, 1Ru-CeO₂NF and CeO₂NF. (The amount of H₂ consumption was calibrated with the H₂ consumption value of Ag₂O as standard.)



Figure 7. (a) Schematic illustration of electrospinning system; (b, c) SEM image (low mag. and high mag.) of electrospun Ce(NO₃)₃/PVP precursor fibers; (d) SEM image of CeO₂NF; (e, f) SEM image (low mag. and high mag.) of electrospun [Ce(NO₃)₃ + Ru(NO)(NO₃)₃]/PVP precursor fibers; (g) SEM image of 1Ru-CeO₂NF catalyst; (h, i) SEM image (low mag. and high mag.) of 1Ru-CeO₂NF catalyst with porous microstructure.



Figure 8. TEM bright field image of (a) CeO₂NF, (b) 1RuO_x-CeO₂NF and (c, d) 1Ru-CeO₂NF catalysts; (e) HRTEM image of 1Ru-CeO₂NF; (f) STEM-HAADF image and STEM-EDS elemental mapping of 1Ru-CeO₂NF catalyst; (g, h) STEM-HAADF image and STEM-EDS line scan of 1Ru-CeO₂NF catalyst; (i) EDS spectrum of 1Ru-CeO₂NF catalyst.



Figure 9. *In situ* DRIFTS spectra of CO chemisorption on (a) commercial RuO₂, (b) 1RuO_x-CeO₂NF, (c) 1Ru-CeO₂NF and (d) CeO₂NF catalysts.

Table 1. BET surface area obtained from N_2 -physisorption, crystallite size and lattice parameter calculated from XRD analysis, the relative Ce³⁺ concentration, the relative content of the surface active oxygen (O_a) and surface Ru species (Ru⁴⁺, Ruⁿ⁺ and Ru⁶⁺) content estimated from XPS results.

Samples	S_{BET} (m ² /g)	Crystallite size (nm)	a(Å)	$Ce^{3+}/(Ce^{3+}+Ce^{4+})$ (%)	$O_a/(O_a+O_l)$ (%)	Ru (%)
RuO ₂	20	18.7	-	-	-	Ru ⁴⁺ : 100%
1RuO _x -CeO ₂ NF	111	5.6	5.4070	25.7	20.6	Ru ⁿ⁺ : 53.3%/Ru ⁶⁺ : 46.7%
1Ru-CeO ₂ NF	117	5.6	5.4082	30.7	24.0	Ru4+: 42.8%/Run+: 57.2%
CeO ₂ NF	116	5.8	5.4100	31.8	34.6	-