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Electron Microscopy Investigation of CeO_2 Nanofibers Supported Noble Metal (Pt, Pd and Ru) Catalysts for CO Oxidation

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With the ever-growing requirements for clean energy production and processing, developing highly efficient catalysts to eliminate environmental pollutants is of vital importance. As one of the remarkable supports or promoters in heterogeneous catalysis, ceria (CeO_2) and related support materials with high oxygen storage-release capacity have been widely investigated [1]. And in recent decades, lots of approaches regarding morphology-controlled synthesis of CeO_2 were employed to tune the catalytic activity of CeO_2 supported catalysts [2]. Herein, we report to synthesize CeO_2 nanofibers (CeO_2NF) via electrospinning technique and prepare a series of CeO_2NF supported noble metal (Pt, Pd and Ru) catalysts. This paper is mainly focused on electron microscopy study of the as-prepared electronspun CeO_2NF support and CeO_2NF supported noble metal catalysts, aiming at exploring the relationship between catalyst-support interfacial structure and the enhanced low temperature CO oxidation activity.

CeO_2NF were fabricated using an electrospinning method (Fig. 1(a), Nanospinner 24, Inovenso), followed by a calcination process. Typically, a 20-mL syringe was used to load the precursor/polymer solutions $Ce(NO_3)_3$/PVP, 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, and sprayed to a grounded rotating drum collector. The processing parameters are 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 ℃ in a drying oven for 12 h. CeO_2NF were finally obtained by annealing the $Ce(NO_3)_3$/PVP precursor fibers in a box furnace at 500 °C for 3 h. For CeO_2NF supported noble metal catalysts, 1 wt.% Pt, Pd and Ru were loaded onto the CeO_2NF by impregnating CeO_2NF with the aqueous solution containing a required amount of $PtCl_4$, $Pd(NO_3)_2$ and $Ru(NO)(NO_3)_3$ for 2 h, respectively. Then the samples were heated at 100 °C on a hot plate to vaporize water and transferred into a drying oven for further drying. After that, the as-prepared dry samples were thermally-treated with a gas flow rate 150 cc/min of 5 vol.% H_2/95 vol.% Ar at 300 °C for 5 h. The structural and composition characterization of different samples were carried out using a Transmission Electron Microscope (TEM, FEI Tecnai F 20), equipped with a high angle annular dark field (HAADF) detector and EDAX energy dispersive X-ray system, which was operated at 200 kV. N_2 physisorption at ~77 K was used to determine the single-point BET surface area of the catalysts. Hydrogen temperature programmed reduction (H_2-TPR) was performed on a chemisorption analyzer (AutoChem II 2920, Micrometrics). The catalytic oxidation of CO was conducted using a fixed bed plug flow reactor system.

From the SEM images in Fig. 1(b) and (c), it is noted that the $Ce(NO_3)_3$/PVP precursor fibers have smooth surfaces and network structure with an average diameter of ~ 200 nm. After being calcined, the fiber-like morphology was retained, but the average diameter of CeO_2NF turned to <100 nm. TEM analysis (Fig. 1(d) and (e)) further revealed the microstructure of CeO_2NF, which consists of small CeO_2 clusters arranging randomly. The HRTEM image (Fig. 1(f)) of CeO_2NF suggests a {111} termination surface of small clusters. H_2-TPR (Fig. 1(i)) was applied to probe the reducibility of pure CeO_2NF as

well as the corresponding catalysts. For pure CeO_2NF, the reduction peak at 463 ℃ is attributed to the reduction of surface Ce^{4+}, whilst the shoulder peak with lower temperature at 350 ℃ could be ascribed to the reduction of the outermost layer of CeO_2NF or surface CeO_2 of very small particle size. After introduction of different noble metals, all the CeO_2NF supported catalysts still remain fibrous structure. The EDS analysis confirms the existence of each noble metal elements, and the STEM-EDS mapping (Fig. 1(k) and associated elemental maps) indicates the elements are well distributed onto the CeO_2NF surface. The H_2-TPR results of the catalysts reveals a strong metal-support interaction between as-loaded noble metals and CeO_2NF support, which lower the reduction peak of Ce^{4+} from 463℃ to 357 ℃, 340 ℃ and 260 ℃ for the supported Pt, Pd and Ru counterparts, respectively. Catalytic oxidation of carbon monoxide (Fig. 1(g) was used to test the activity of the catalysts, and the catalytic performance can be ranked as: 1% Ru/CeO_2NF ≈ 1% Pd/CeO_2NF > 1% Pt/CeO_2NF > pure CeO_2NF. Besides, the BET surface area of all aforementioned show the value of > 100 m^2/g, which can be ascribed to the porous and rough surface of CeO_2NF as observed from the TEM image (Fig. 1(e)). One interesting finding worthy to be pointed out is that from the STEM-EDS line scan result (Fig. 1 (g) and (h)), some CeO_2NF supported catalyst has hollow structure which shows better catalytic activity. In addition, more detailed atomic level structure and composition information at the interfaces will be presented.

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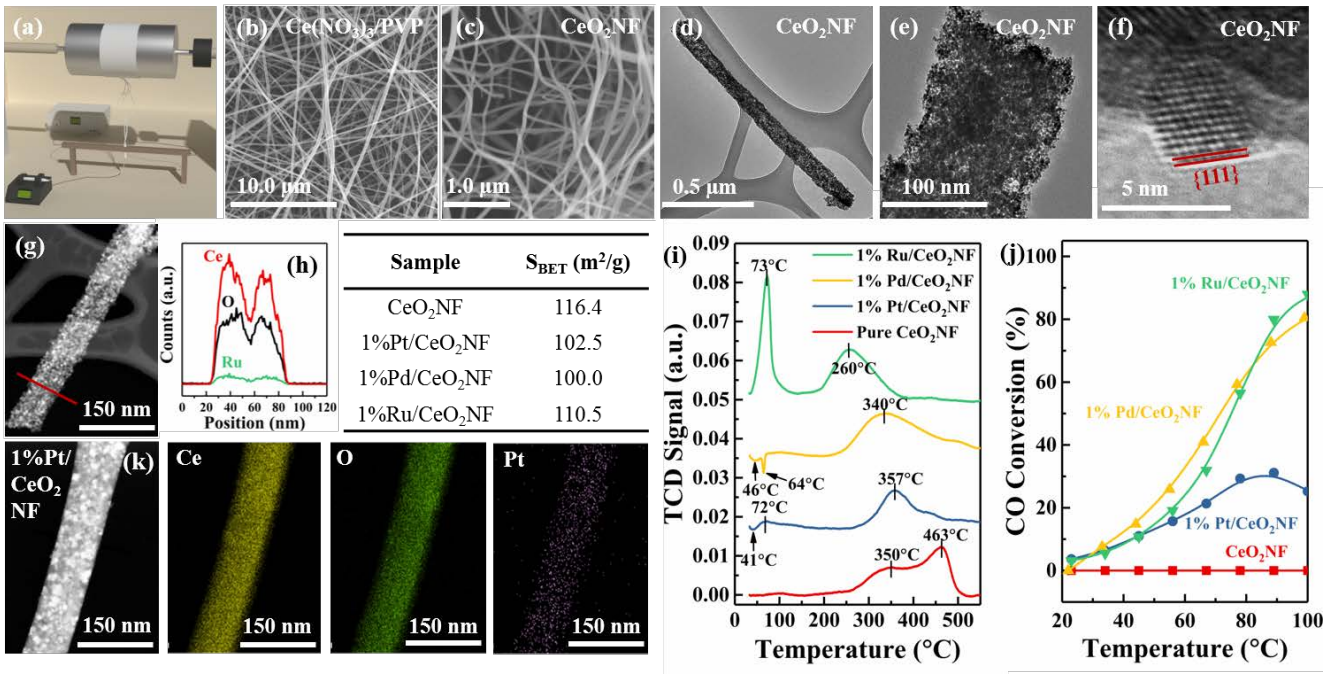

Figure 1. Schematic diagram of electrospinning system (a); SEM image of $Ce(NO_3)_3$/PVP precursor (b) and CeO_2NF (c); TEM bright field (d, e) and HRTEM images (f) of CeO_2NF; STEM-HAADF image (g) and line scan spectrum of 1%Ru/CeO_2NF (h); H_2-TPR profiles (i) and CO catalytic performance (j) CeO_2NF and CeO_2NF supported noble metal (Pt, Pd and Ru) catalysts; STEM-EDS elemental mapping of 1%Pt/CeO_2NF (k); and BET surface area.

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