

A Highly Reactive and Sinter-Resistant Catalytic System Based on Platinum Nanoparticles Embedded in the Inner Surfaces of CeO₂ Hollow Fibers**

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The catalytic properties of a supported system are strongly dependent on the types of metal and supporting material involved.^[1–4] Platinum nanoparticles (NPs) supported on ceria (CeO₂) have shown higher catalytic activities for a wide variety of reactions, including water-gas shift,^[5,6] CO oxidation,^[7] and hydrogenation^[8,9] when compared to those supported on other oxides. Therefore, CeO₂ has been widely employed as a support for manufacturing automotive catalysts because of its peerless oxygen storing/releasing capabilities as well as its superior ability to stabilize noble metals.^[10,11] In particular, Pt/CeO₂ catalysts are known to exhibit strong metal–support interaction effects with a potential to enhance the catalytic activities for reactions involving rapid oxygen and/or electron transfer between the metal and the support.^[12–15] Although there are many benefits in utilizing the Pt/CeO₂ system in real-world catalytic applications, great challenges, such as low thermal stability and loss of catalytic activity owing to sintering, still need to be addressed. In catalysts for automotive exhaust treatment, these problems are partially mitigated by combining CeO₂ with ZrO₂ in a solid solution, but precious metal sintering remains a primary deterioration mechanism.

The use of nanostructured composite materials is one strategy to address the sintering issue. Yan and co-workers recently synthesized CeO₂ nanoparticles covered with Pt NPs

and then SiO₂ shells to protect the PtNPs from aggregation during calcination,^[16] but their approach required multiple steps to generate the SiO₂ shells and then dissolve them. As a major drawback, the Pt/CeO₂ nanocomposites could only withstand calcination up to 450 °C after the removal of the SiO₂ shells. Tsang and co-workers demonstrated the synthesis of a Pt/CeO₂ core–shell NPs by a modified microemulsion method.^[17,18] The resultant catalyst showed significantly improved catalytic activity and selectivity in water-gas shift over methanation by controlling the thickness of the CeO₂ protective layer. However, the Pt/CeO₂ core–shell NPs exhibited considerable aggregation in the reaction medium, which may negatively impact their catalytic activity in a practical application.

Herein, we report a simple, template-based procedure for the fabrication of CeO₂ hollow fibers with PtNPs embedded in the inner surfaces (Figure 1). The first step involved the

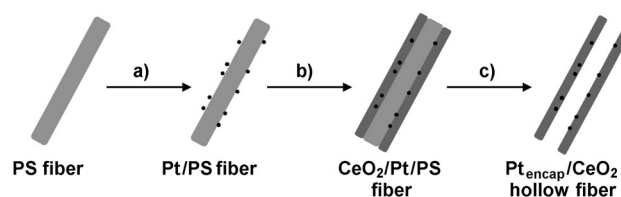


Figure 1. The three-step procedure developed herein for the preparation of Pt_{encap}/CeO₂ hollow fibers with open ends. a) Deposition of Pt NPs; b) coating of CeO₂ sheath; c) removal of PS fiber at 400 °C. Pt_{encap}/CeO₂ designates a CeO₂-supported Pt catalyst in which the PtNPs are almost completely encapsulated by CeO₂.

generation of polystyrene (PS) fibers by electrospinning, followed by plasma treatment to render their surfaces hydrophilic for the deposition of Pt NPs. The deposited Pt NPs then served as nucleation sites to initiate the growth of a uniform sheath of CeO₂ on the surface of each PS fiber. After the removal of PS fibers by calcination in air at 400 °C, we obtained CeO₂ hollow fibers with inner surfaces that were embedded with PtNPs. In addition to a porous wall, the hollow fiber also had open ends to ensure high permeation and mass transfer rates for species involved in a catalytic reaction. The turnover frequency (TOF) of this new catalytic system for CO oxidation was found to be 2–3 orders of magnitude higher than those of other systems. Thanks to an effective metal–support contact, it was also thermally stable against sintering up to 700 °C.

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The nonwoven mat of PS fibers was prepared by electrospinning a 20 wt% solution of PS in a mixture of tetrahydrofuran (THF) and dimethylformamide (DMF) at a mass ratio of 1:1. The average diameter of the as-spun PS fibers was $1.16 \pm 0.22 \mu\text{m}$ (Supporting Information, Figure S1a). The PtNPs stabilized by poly(vinyl pyrrolidone) (PVP) were prepared using a method based on polyol reduction.^[19] The as-synthesized PtNPs were uniform in size (Figure S1b), with an average diameter of 3.5 nm (Figure S1c). The surface of a plasma-treated PS fiber could be easily coated with the PtNPs by immersing the fiber mat in a suspension of PtNPs in ethanol, followed by washing to remove the loosely bound NPs and drying in air (Figure S1d).

The PS fiber decorated with PtNPs was then employed as a substrate for the in situ growth of a CeO_2 sheath by a process involving reaction of cerium(III) acetate with 6-aminocaproic acid (6ACA) in an aqueous medium in air.^[20] As shown in Figure 2a, the CeO_2 coating was deposited

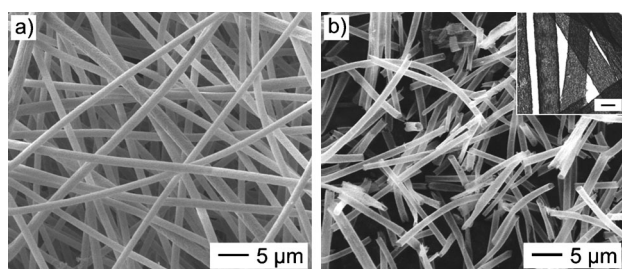


Figure 2. SEM images of PS fibers with surfaces that have been coated with PtNPs and then CeO_2 sheaths a) before and b) after calcination in air at 400°C for 2 h. (Inset: TEM image confirming the hollow structure; scale bar: $1 \mu\text{m}$).

uniformly on the surface of each Pt/PS fiber and no interfiber connection was observed. The average diameter of the CeO_2 /Pt/PS fibers increased to $1.37 \pm 0.30 \mu\text{m}$. From the SEM data, the thickness of the CeO_2 sheath was estimated to be about 100 nm in thickness. Based on an XRD pattern (Supporting Information, Figure S2a), the as-deposited CeO_2 coating was crystallized in a cubic fluorite structure ($Fm\bar{3}m$, $a = 5.411 \text{ \AA}$, JCPDS Card No. 34-0394). It is remarkable that a complete sheath made of crystalline CeO_2 nanoparticles could be formed on the PS fiber under relatively mild reaction conditions (60°C for 2 h). In this case, the PtNPs played an important role in the nucleation and growth of CeO_2 nanocrystals in the presence of 6ACA. Because the PVP-stabilized PtNPs were negatively charged with a zeta potential of -0.83 mV under a slightly basic pH (7.5), the Ce^{3+} cations could easily adsorb onto the PtNPs to facilitate the nucleation and growth of CeO_2 nanocrystals. Although the details for CeO_2 growth still need to be fully investigated, our TEM observations did provide some evidence to support this proposed mechanism. The organic components in the as-prepared CeO_2 /Pt/PS structures, including PS, PVP, and 6ACA, could be removed by calcination in air at an elevated temperature to generate CeO_2 hollow fibers with PtNPs embedded in the inner surfaces. The SEM image in Figure 2b and the TEM image in the inset clearly show a hollow

structure for the CeO_2 fibers. The loading of Pt in the as-prepared $\text{Pt}_{\text{encap}}/\text{CeO}_2$ hollow fibers was about 0.98%, as determined by inductively coupled plasma mass spectrometry (ICP-MS).

Figure 3 shows TEM images of the $\text{Pt}_{\text{encap}}/\text{CeO}_2$ hollow fibers after they had been further treated at different temperatures in air for 2 h. The products obtained at 400 and 800°C

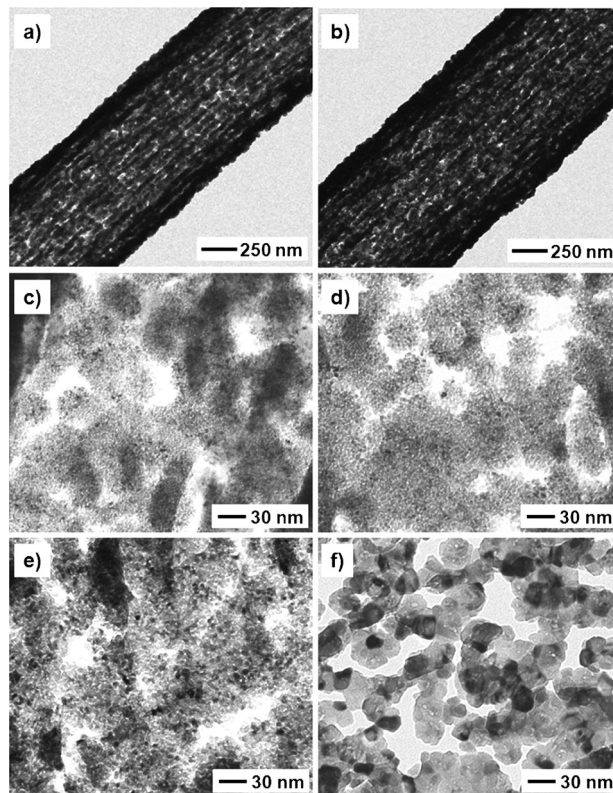


Figure 3. a), b) Low-magnification TEM images showing a $\text{Pt}_{\text{encap}}/\text{CeO}_2$ hollow fiber after it had been calcined in air for 2 h at a) 400 and b) 800°C . c)–f) High-magnification TEM images revealing the wall structures of the $\text{Pt}_{\text{encap}}/\text{CeO}_2$ hollow fibers after calcination in air for 2 h at c) 400 , d) 600 , e) 700 , and f) 800°C .

still maintained a tubular structure without being collapsed, demonstrating a rather good thermal stability for the relatively thin CeO_2 sheath. Furthermore, the PtNPs were effectively prevented from sintering up to 700°C as a result of the CeO_2 barrier surrounding each PtNP. At 800°C (Figure 3f), both sintering of PtNPs and growth of CeO_2 crystallites started to occur, which was manifested by the formation of Pt large agglomerates and a substantial increase in grain size for CeO_2 . The X-ray powder diffraction pattern (Supporting Information, Figure S2a) taken from these samples confirmed that the CeO_2 phase remained to be in a cubic fluorite structure. For the product obtained at 800°C , a weak peak at 39.6 degrees appeared, which could be assigned to the (111) diffraction of Pt, indicating the formation of Pt large agglomerates by sintering. The changes in size for the embedded PtNPs (measured from the TEM images) and the CeO_2 crystallites (derived from the XRD patterns using the Debye–Scherrer equation) after the samples had been

treated in air at different temperatures are shown in the Supporting Information, Figure S2b. Up to 400 °C, no significant change in size was observed for both the PtNPs and CeO₂ crystallites. When the temperature was increased from 400 to 700 °C, the average sizes of the PtNPs and CeO₂ crystallites were increased from 3.5 to 4.1 nm and from 3.2 to 5.1 nm, respectively. As the temperature was further increased to 800 °C, the PtNPs grew to 12 nm and the CeO₂ crystallites also grew to 11.2 nm, which is more than triple relative to their original sizes. The missing diffraction peak at 39.6° for Pt for all the samples until 700 °C also suggested that the new Pt_{encap}/CeO₂ system could resist thermal sintering up to this temperature. Above 700 °C, the simultaneous sintering of CeO₂ crystallites may have induced and facilitated sintering of the PtNPs, leading to a quick increase in size for the PtNPs. We also tried to resolve possible changes to the morphology of PtNPs and the platinum–oxide interface by high-resolution TEM (Supporting Information, Figure S3), but it was very difficult to obtain any meaningful data owing to the presence of a polycrystalline CeO₂ matrix around each PtNP.

We measured the surface areas of the PtNPs embedded in the Pt_{encap}/CeO₂ hollow fibers by CO titration of chemisorbed oxygen (Supporting Information, Table S1). The titrations were performed at –20 °C to minimize oxygen spillover to Pt sites from CeO₂. For the samples treated at 400, 600, 700, and 800 °C in air for 2 h, the accessible Pt surface areas and the corresponding Pt dispersions were found to be in the ranges of 0–3.4 m² g^{–1} and 0–1.7 %, respectively. Unexpectedly, CO titration failed to give a measurable Pt surface area and dispersion for the Pt_{encap}/CeO₂ sample calcined at only 400 °C. It is possible that organic residues from the incomplete combustion of PVP and PS might have blocked the channels in the CeO₂ sheath so that the O₂/CO analytes could not access the surface of PtNPs. After calcination at 600 °C, which presumably allowed more of the organic residues to be burned away, CO titration gave a Pt surface area of 2.6 m² g^{–1} and dispersion of 1.2 %. The highest accessible Pt surface area (3.4 m² g^{–1}) and dispersion (1.7 %) were obtained after calcination at 700 °C. By further increasing the calcination temperature to 800 °C, the surface area and dispersion dropped to 0.8 m² g^{–1} and 0.4 %, respectively, which is consistent with the sintering of PtNPs observed by TEM and XRD.

Figure 4 compares the TOFs of CO oxidation reaction obtained for two samples of Pt_{encap}/CeO₂ hollow fibers and a Pt/SiO₂ catalyst reported by Cant and co-workers.^[21] The Pt/SiO₂ TOFs fit the same Arrhenius curve extrapolated from higher-temperature measurements under the same conditions on clean Pt(100) and clean, well-defined Pt nanoparticles of different sizes supported on planar SiO₂ substrates,^[22] and thus represent the expected structurally insensitive activity of normal Pt sites. Also shown are TOFs for a Pt/TiO₂ catalyst prepared in the same way as the structure shown in Figure 2b,^[23] with a Pt dispersion of 31 % by CO titration. These TOFs are almost identical to Pt/SiO₂, as expected for the normal metallic Pt sites. The Pt_{encap}/CeO₂ hollow fibers exhibited TOFs three orders of magnitude higher than those of the Pt/SiO₂ and Pt/TiO₂ catalysts within the

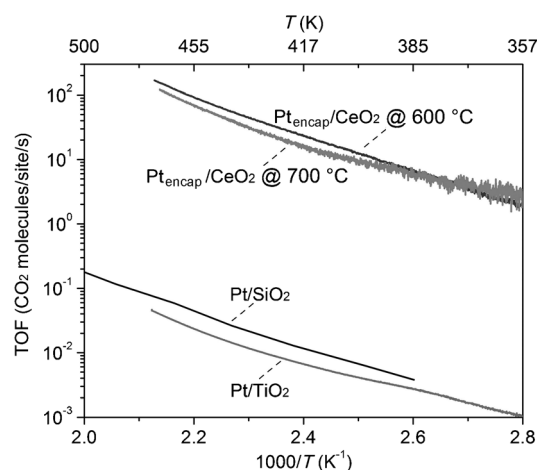


Figure 4. Turnover frequencies (TOFs) at an O₂/CO ratio of 1:2 versus temperature for Pt_{encap}/CeO₂ hollow fibers calcined at 600 and 700 °C for 2 h. For comparison, TOFs are also shown for a conventional Pt/SiO₂ catalyst (5 wt % Pt), as reported by Cant and co-workers^[21] under the same reaction conditions. As discussed in the text, this Pt/SiO₂ catalyst had TOFs similar to those of a clean Pt(100) surface. They were also nearly identical to the TOFs obtained for a Pt/TiO₂ catalyst under the same conditions, confirming that the TOFs of the Pt/SiO₂ were as expected for normal metallic Pt sites, and that the new Pt_{encap}/CeO₂ system was 1000-fold faster.

comparable temperature range of 384–476 K, providing a direct evidence to support its far superior catalytic activity. These TOFs were calculated based on the Pt dispersion measured by CO titration (Supporting Information, Table S1), which were essentially unchanged after these catalytic rate measurements (not shown), but which were about 10-fold less than what was measured from the size of the PtNPs using TEM. Even considering the worst possible experimental errors in dispersion, the activity of the Pt_{encap}/CeO₂ hollow fibers was still more than 100-fold higher than the Pt/SiO₂ and clean Pt model catalysts. Also, if we used the average particle size of 4.1 nm measured by TEM after calcination at 700 °C to calculate the Pt surface area (assuming no poisoned Pt sites), it gave 40 m² of Pt. Based on this area, we still calculate a TOF that was ca. 100-fold higher than that of the Pt/SiO₂. Moreover, it is worth pointing out that the Pt/SiO₂, Pt/Al₂O₃, and Pt/CeO_x/Al₂O₃ catalytic systems studied by other groups^[24] all exhibited much lower TOFs than that of Pt_{encap}/CeO₂ hollow fibers under the same conditions with O₂/CO₂ ratio = 0.5. In studies of CO oxidation over traditionally prepared Pt/CeO₂ catalysts, it was reported that the CO oxidation activity of Pt, which ended up partially covered and/or encapsulated by a thin layer of CeO₂, was higher than that of Pt itself.^[17,25,26] However, those prior studies only showed a 3–4-fold increase in TOF, which is much less than the 1000-fold increase observed here. The CeO₂ layer on Pt was suggested to accelerate the overall reaction rate by participating in accepting and donating oxygen atoms, which compensated the limited accessibility of reactants to the catalytic sites.^[27,28] A roughly 100-fold increase in Pt activity owing to CeO₂ was reported when the CO/O₂ ratio was about 1000, which could be attributed to oxygen spillover to the Pt from the CeO₂ if the Pt sites were too saturated by

CO to dissociate O₂, but no increase owing to CeO₂ was observed in that study at the stoichiometric ratio used here.^[29] For the hollow Pt_{encap}/CeO₂ fibers described here, the CeO₂ nanocrystalline sheath tightly surrounding the PtNPs with a maximized Pt–CeO₂ interface greatly benefitted the catalytic CO oxidation rate. Further studies on the mechanism of CO oxidation using the Pt_{encap}/CeO₂ system are required to understand this phenomenon.

In summary, we have demonstrated a method for embedding Pt NPs in the inner surfaces of CeO₂ hollow fibers with open ends to generate a new catalytic system that could resist thermal sintering up to 700 °C. The TOF of the as-synthesized Pt_{encap}/CeO₂ hollow fibers for CO oxidation was 2–3 orders of magnitude higher than those based on the conventional Pt/SiO₂ catalytic system, which could be attributed to a unique structure and composition for maximizing the Pt_{encap}/CeO₂ interface. Future work will involve the introduction of a protective layer based on oxides, such as SiO₂ or Al₂O₃, to the Pt_{encap}/CeO₂ catalytic system to achieve high reactivity and sintering resistance at temperatures even higher than 700 °C.

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