



Fabrication of Pt/CeO₂ nanofibers for use in water–gas shift reaction

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ABSTRACT

The Pt/CeO₂ nanofibers with diameter of 80–120 nm were prepared by electrospinning method with Ce(NO₃)₃·6H₂O as raw material and PVP as spinnable additive. This method included the preparation of spinnable sol and electrospinning process. After calcination at 400 °C, the fluorite structure Pt/CeO₂ nanofibers with loose structure were obtained, which were composed of 5–10 nm particles. In the water–gas shift reaction, 1 wt.% Pt doped CeO₂ nanofibers exhibited superior catalytic activity compared with pure CeO₂ nanofiber, Pt loaded CeO₂ powder and Pt loaded CeO₂ nanofiber, and the CO conversion reaches 98% at 320 °C and maintains that until 360 °C, showing potential application in water–gas shift reaction.

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1. Introduction

Fuel cell has wide applications in fixed and mobile power for its high energy conversion efficiency and environmental protection. The water–gas shift reaction for the preparation of hydrogen in fuel cells becomes the hot topic, and the research on the water–gas shift catalysts is the most important. The reaction process includes the adsorption of H₂O and oxidation of CO as well as the decomposition of the H₂O on the catalyst. The metals Pt, Pd, Au, Ag, Ru and Cu exhibit good adsorption capacity for CO, and can be used as the active components to activate CO. Some oxides such as CeO₂, Fe₂O₃, La₂O₃ and ZrO₂ can produce steady-state adsorption oxygen atoms under certain conditions, which can oxidize the CO to produce the free hydrogen. Thus these metals (Pt, Pd, Au, Ru, Cu, Ag) loading on the oxide supports (CeO₂, TiO₂, ZrO₂, etc.) could form the catalysts for the water–gas shift reaction [1,2].

The metal loaded CeO₂ has been applied as the catalyst in water gas shift reaction [3,4]. Of these catalysts, the supported Pt is a potential one for its good stability and high activity [5,6]. The reported Pt/CeO₂ catalyst is usually granular powder, and prepared by immersing CeO₂ in Pt based solution and then calcined [7–9]. This method always needs repeated drying and calcination, and the particle-size and the distribution of Pt metal in catalyst are not uniform, resulting in the poor stability of catalytic property. In addition, it is difficult to maintain a good performance for the powder catalysts as they are fixed, recycled and reused. Electrospinning fibers can solve the above problems to some extent.

In recent years, there are some reports on the preparation of nanofibers such as CeO₂ [10–13], Pd/SnO₂ [14,15], Pd/TiO₂ [16], and Pd/ZnO [17] by electrospinning method, and the precious metals loaded oxides nanofibers show good catalytic performance and stability. However, the precious metals doped CeO₂ nanofiber for catalyzing the water gas shift reaction has not been reported. In this research, Pt/CeO₂ nanofibers were fabricated by a simple electrospinning technology, which exhibited high catalytic activity in the water gas shift reaction.

2. Experimental section

In a typical preparation, 1.0 g Ce(NO₃)₃·6H₂O and 11.0 mg H₂PtCl₆·6H₂O were dissolved into 2.0 mL deionized water under vigorous stirring to form a transparent solution. Then the solution was added to the mixture of 8.0 mL ethanol and 4.0 mL deionized water containing 0.5 g polyvinylpyrrolidone (PVP, M_w = 1300000). After 4.0 h of stirring, the transparent electrospinnable sol was formed.

The sol was transferred into a hypodermic syringe with 10.0 mL capacity. A variable high-voltage power supply was connected to the needle tip of the syringe and a stainless steel collector. The applied voltage was 20 kV, and the distance between the needle tip and the collector was 20 cm. The as-spun gel fibers were calcined in air from room temperature to 400 °C at 1.0 °C/min and maintained at that temperature for 3 h. The concentration of Pt in the final product was 1 wt.%. The CeO₂ nanofibers were also prepared without adding H₂PtCl₆·6H₂O.

Thermal gravimetric (TG) analysis was carried out from 20 °C to 600 °C at 10.0 °C/min under air atmosphere (Mettler Toledo, TGA/SDTA 851^o). The infrared (IR) spectra were recorded on a Nicolet 5DX-FTIR spectrometer using KBr pellet method. The X-ray diffraction (XRD) patterns of the samples were collected on a Rigaku D/Max 2200PC diffractometer with a graphite monochromator and CuKα

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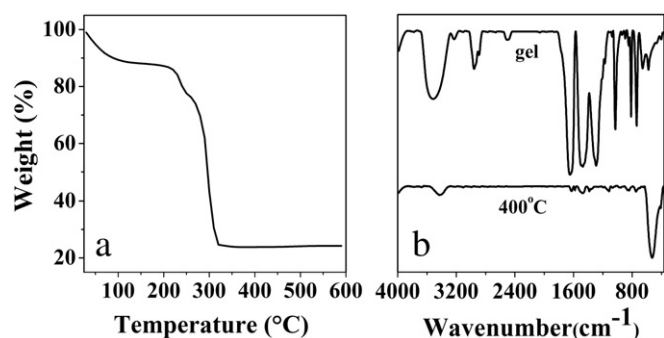


Fig. 1. (a) TG curve of the gel fibers and (b) IR spectra of the gel fibers and those after calcination.

radiation ($\lambda = 0.15418$ nm). The morphology and microstructure of the products were characterized using a field emission scanning electron microscope (FE-SEM, JSM-6700F) and a high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2100).

The catalytic property of the fiber for the water–gas shift reaction was carried out in the gas evaluation device. Water was pumped into the vaporization chamber by high-precision micro-injection, and the mixture of water vapor, CO and N₂ flew through catalyst in the center of quartz tube. The reaction product passed through gas-phase infrared detector after dried by silica gel, and the contents of CO, CO₂ and H₂ were obtained correspondingly. The amount of the catalyst was 100.0 mg and the reactant gas at a flow rate of 100.0 mL/min consisted of 2.0 vol.% CO, 10.7 vol.% H₂O and 87.3 vol.% N₂.

3. Results and discussion

In the preparation, the mixture of ethanol and deionized water was used as solvent, and PVP was added as spinning additive to increase the spinnability of the sol. Increasing the proportion of low boiling point ethanol can effectively improve the spinning speed, but it leads to the flocculation of PVP and Ce(NO₃)₃ in the solution. Here, the mixture of water and ethanol with volume ratio of 1:2 was selected as solvent to ensure that all components are completely dissolved.

From Fig. 1a, the weight of the gel fiber reached constant after 340 °C, indicating that all the organics had been removed and the Pt/CeO₂ content in gel fiber was about 25%. Based on the TGA result and considering the temperature error during heating in the muffle furnace, the gel fibers were calcined at 400 °C to fully remove the organics. From the IR spectrum of the gel fibers (Fig. 1b), the absorptions around 3460 cm⁻¹ and 1650 cm⁻¹ were assigned to the stretching and bending vibrations of hydroxyls. Those at 2950 cm⁻¹ and 2890 cm⁻¹ were attributed to the stretching vibrations of C–H from –CH₃ and CH₂ in PVP. The characteristic peaks of PVP were from 1700 cm⁻¹ to 1020 cm⁻¹, and absorptions from 840 cm⁻¹ to 815 cm⁻¹ were assigned to NO₃⁻. After being calcined at 400 °C, the strong absorption at 530 cm⁻¹ was attributed to the stretching vibration of Ce–O in CeO₂, and that from 1520 cm⁻¹ to 1432 cm⁻¹ almost disappeared, indicating the removal of organics.

From the SEM images of CeO₂ and Pt/CeO₂ nanofibers (Fig. 2), the diameter of the as-prepared nanofibers ranges from 80 nm to 120 nm with coarse surface. There is no significant difference between the CeO₂ and Pt/CeO₂ fibers. HR-TEM observations (Fig. 2e, f) indicate that the nanoparticles arrange randomly in the fiber. The lattice spacing, ca. 0.27 nm, is consistent with the {200} interplanar spacing of CeO₂, and the lattice spacing of ca. 0.20 nm is close to that of {200} plane of fcc Pt. The grain size of Pt is estimated to be ca. 4.5 ± 0.5 nm from the HR-TEM image (denoted by white circle in Fig. 2f). From the lattice fringes, it is concluded that the size of the CeO₂ nanoparticles composed the Pt/CeO₂ fibers is 5–10 nm.

Fig. 3 shows XRD patterns of the CeO₂ and Pt/CeO₂ nanofibers. The reflections match well with the cubic fluorite structure CeO₂ (JCPDS No.34-0394). As to Pt-doped sample, there is no indication of the presence of any dopant, which might be due to the low content and small particle size of the doped Pt in the fibers. Based on (111) reflections, the average crystallite sizes in CeO₂ and Pt/CeO₂ nanofibers calculated by the Scherrer's equation are 7.6 nm and 7.8 nm, which indicates that the introduction of Pt has little effect on the crystallite size of CeO₂, and this is consistent with the HRTEM observation.

The catalytic performance for water–gas shift reaction was tested. For this exothermic reaction, lower temperature is conducive to the shift reaction, but it leads to a slow reaction rate. Therefore, the right temperature is necessary to achieve a good catalytic performance. In this test, the temperature was chosen from 170 °C to 360 °C, and the catalytic conversion was obtained by detecting the CO flow.

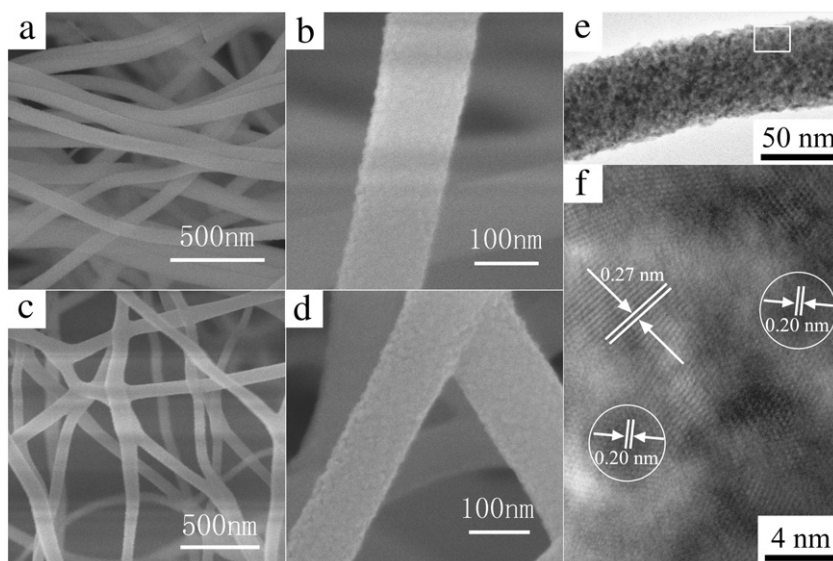


Fig. 2. SEM (a–d) and HR-TEM images (e, f) of CeO₂ (a, b) and Pt/CeO₂ (c–f) nanofibers.

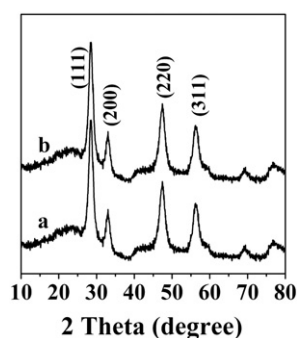


Fig. 3. XRD patterns of CeO_2 (a) and Pt/CeO_2 (b) nanofibers.

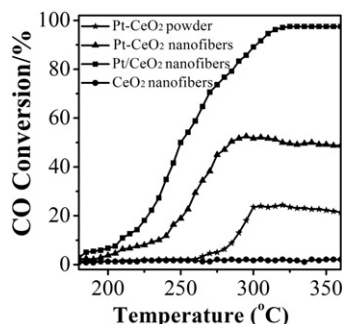


Fig. 4. Temperature dependence of CO conversion for water–gas shift reaction with different catalysts.

As shown in Fig. 4, for Pt/CeO_2 nanofiber catalyst, the CO conversion increases with the temperature, and it increases rapidly with the temperature higher than 205 °C. As the temperature goes up to 320 °C, the CO conversion reaches the maximum of 98% and maintains that until 360 °C. While pure CeO_2 nanofiber is used as catalyst, the CO conversion is only 2–3% in the whole reaction process. As references, the Pt-CeO_2 powder and the Pt-CeO_2 nanofibers were obtained by impregnating the CeO_2 powder and the prepared CeO_2 nanofibers with H_2PtCl_6 solution, followed by drying and calcinations, in which the Pt contents were as same as that in the Pt/CeO_2 nanofibers. As to Pt-CeO_2 nanofibers catalyst, the CO conversion is 52% when the

temperature reaches 290 °C, and 23% CO is converted at 300 °C with Pt-CeO_2 powder as catalyst. If the reaction temperature further increases, the activities of catalysts prepared by impregnation decrease. The prepared Pt/CeO_2 nanofibers exhibit superior catalytic performance for the lower catalytic temperature and higher CO conversion, showing potential application in water–gas shift reaction.

4. Conclusions

Pt/CeO_2 nanofibers were synthesized through an electrospinning method followed by calcination. The electrospun Pt/CeO_2 nanofibers exhibited good catalytic activity in water–gas shift reaction with the CO conversion that reached 98% at 320 °C and maintained that until 360 °C, showing potential application in the future.

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References

- [1] Farias AD, Nguyen-Thanh D, Fraga MA. *Appl Catal B Environ* 2010;93:250–8.
- [2] Andreeva D, Idakiev V, Tabakova T, Ilieva L, Falaras P, Bourlinos A, et al. *Catal Today* 2002;72:51–7.
- [3] Li Y, Fu Q, Flytzani-Stephanopoulos M. *Appl Catal B Environ* 2000;27:179–91.
- [4] Bunluesin T, Gorte RJ, Graham GW. *Appl Catal B Environ* 1998;15:107–14.
- [5] Panagiotopoulou P, Kondarides DI. *Catal Today* 2006;112:49–52.
- [6] Farias AD, Bargiela P, Rocha MG, Fraga MA. *J Catal* 2008;260:93–102.
- [7] Panagiotopoulou P, Papavasiliou J, Avgouropoulos G, Ioannides T, Kondarides DI. *Chem Eng J* 2007;134:16–22.
- [8] Hwang K, Ihm S, Park J. *Fuel Process Technol* 2010;91:729–36.
- [9] Han W, Wen W, Hanson JC, Teng X, Marinkovic N, Rodriguez JA. *J Phys Chem C* 2009;113:21949–55.
- [10] Yang X, Shao C, Liu Y, Mu R, Guan H. *Thin Solid Films* 2005;478:228–31.
- [11] Cui Q, Dong X, Wang J, Li M. *J Rare Earths* 2008;26:664–9.
- [12] Luepong K, Koombhongse P, Kongkachuichay P. *Chiang Mai J Sci* 2009;37:85–91.
- [13] Zhang H, Li Z, Liu L, Xu X, Wang Z, Wang W, et al. *Sens Actuators B* 2010;147:111–5.
- [14] Choi J, Hwang I, Kim S, Park J, Park S, Jeong U, et al. *Sens Actuators B* 2010;150:191–9.
- [15] Moon J, Park J, Lee S, Zyung T, Kim I. *Sens Actuators B* 2010;149:301–5.
- [16] Wei S, Yu Y, Zhou M. *Mater Lett* 2010;64:2284–6.
- [17] Panagiotopoulou P, Kondarides DI. *J Catal* 2004;225:327–36.