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Fabrication of CeO_2 nanotube supported Pt catalyst encapsulated with silica for high and stable performance

Chao Wan[a,b], Dang-guo Cheng [b,*], Fengqiu Chen [a,b] and Xiaoli Zhan [b]

[a] *Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Zhejiang University, 38 Zheda Road, Hangzhou 310027, China*

[b] *College of Chemical and Biological Engineering, Zhejiang University, 38 Zheda Road, Hangzhou 310027, China*

* **Corresponding Authors**

E-mail address: dgcheng@zju.edu.cn (D.G. Cheng). Tel.: +86 571 8795 3382. Fax: +86 571 8795 1227.

1 Catalysts preparation

Synthesis of CeO_2 nanotube: CeO_2 nanotube was prepared by hydrothermal synthesis method using polymer template based on previous report. Typically, 5.8 g of $(EO)_{20}(PO)_{70}(EO)_{20}$ triblock copolymer (P123) (Aldrich, AR,M=5800) was dissolved in 20mL anhydrous ethanol (AR) and 20mL deionized water at room temperature, after the dissolution of P123, 1.86 g $CeCl_3{\cdot}7H_2O$ (Aldrich, AR) was added into the above solution with vigorous stirring for about 30 min. Next, 3 mL certain ammonium hydroxide (NH_4OH, Sinopharnm Chemical Reagent Co., Ltd, AR) was added into above solution with vigorous stirring for several minutes, and then loaded into a 100 mL PTFE autoclave. The autoclave was placed in an oven and maintained at 160 ºC for 72 h, and then it was cooled to ambient temperature naturally. The precipitate was collected and washed repeatedly with absolute ethanol. The mixture was dried for 2 h in 110 ºC and then the solid was calcined at 550 ºC in the air for 6 h.

Synthesis of PtNPs: Pt NPs of 3-4 nm in diameter were synthesized using a polyol reduction method. While 35 mL of ethylene glycol (EG) was heated at 110 ºC for 30 min, poly (vinyl pyrrolidinone)(PVP) (45 mg, M_w≈55,000, Sigma-Aldrich) and H_2PtCl_6(33mg, Sinopharnm Chemical Reagent Co., Ltd,) were dissolved separately in 4 mL of EG at room temperature. Next, each solution was added simultaneously into the pre-heated EG at a rate of 0.67 mL/min. The reaction was continued under magnetic stirring (200-600 rpm) at 110 ºC for 4 h and finally cooled to room temperature. The as-prepared Pt NPs were collected by vacuum rotary evaporation, washed with ethanol, and then re-dispersed in 40 mL ethanol, which was used as a stock solution of Pt NPs for all the following experiments.

Functionalization of CeO_2 or CeO_2 nanotube with Pt nanoparticles. For Pt/ CeO_2 nanotube, 1.0 g of CeO_2 nanotube were dispersed in 40 mL ethanol by sonification, and then the above-prepared Pt was added into CeO_2 nanotube ethanol solution and stirred for 22 h. Pt/ CeO_2 nanotube was acquired by centrifuging at 55,000 rpm. All of the as-prepared Pt/ CeO_2 nanotube were washed with ethanol for six times. In the case of the preparation of Pt/ CeO_2, the procedure was same as the one of Pt/ CeO_2 nanotube except the support of CeO_2.

Formation of porous SiO_2 sheaths.1 g of the Pt/CeO_2 or Pt/CeO_2 nanotube was dispersed in 100mL of ethanol followed by adding 0.4 g of cetyltrimethylammonium bromide (CTAB, Sinopharnm Chemical Reagent Co., Ltd, 99%), 1 mL of tetraethyl orthosilicate (TEOS, Sinopharnm Chemical Reagent Co., Ltd, 99.999%) and 50 mL of ammonium hydroxide (NH_4OH, Sinopharnm Chemical Reagent Co., Ltd,) and stirred at room temperature for 20 min. The products were collected by centrifugation, washing with ethanol three times and calcination. The final product was referred to as Pt/CeO_2 @SiO_2 or Pt/CeO_2 nanotube@SiO_2.

2. Activity tests

Catalytic tests were conducted at the atmospheric pressure in a quartz fixed-bed reactor (Φ8 × 30 mm) loaded with 0.05 g catalysts (20-40 mesh) mixed with 1 ml of quartz particles. The catalysts were pre-treated with flowing Ar for 1 h at 450 ºC. No other activation procedures (e.g., reduction) were necessary since the catalyst was reduced in situ under the WGS reaction conditions employed. The total gas flow rate under reaction conditions was 80 mL min−1to ensure a gas hourly space velocity (GHSV) of~75 000 mL g−1h−1. The feed gas for the WGS reaction was 1.0 vol % CO and 3.0 vol % H_2O, diluted in Ar. This gaseous mixture was introduced into the reactor at 250°C for 2 h. Aging treatments were performed by heating the sample in the WGS environment at temperatures up to 450°C for 6 h. Subsequently, the sample was cooled down to 250°C in the WGS environment, and the activity was measured again. All heating and cooling rates were 5 °C min−1. Reactants and products were analyzed using a mass spectrometer

(Hiden QIC-20).

The conversion of CO was defined as follows:

CO conversion(%)=$[CO_2]_{outlet}/[CO]_{inlet}*100$

3. Characterization method

Pt loading was determined by Inductively Coupled Plasma Mass Spectrometer (ICP-MS). X-ray powder diffraction (XRD) patterns of the catalysts were recorded on XRD 6000 equipped with Cu Kα radiation at 40kV and 30mA. Transmission electron microscope (TEM) images were obtained on a FEI Tecnai G2 F20 S-TWIN transmission electron microscope at 200 kV. The surface area, pore volume, average pore diameter of the catalysts were measured using N_2 as a sorbate at 77 K in a static volumetric apparatus (Micromeritics ASAP2020).

4. Results

Table S1. Textural properties of the catalysts

Sample	Surface area [a] ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Average pore [b] diameter(nm)	TOF (s^{-1})[c]	Reference
CeO_2 nanotube	56.6	0.20	14.2	-	This work
Pt/ CeO_2	2.5	0.02	33.1	0.11	This work
Pt/ CeO_2 nanotube	38.1	0.20	20.9	0.46	This work
Pt/ CeO_2 nanotube@SiO_2	30.7	0.12	15.1	0.48	This work
Pt/Al_2O_3	-	-	-	0.9×10^{-2}	J. Catal., 2012, 286, 279.

[a] According to BET theory; [b] According to BJH theory; [c]TOF (s^{-1}) has been defined as the number of CO molecules converted per active metal site and per second.

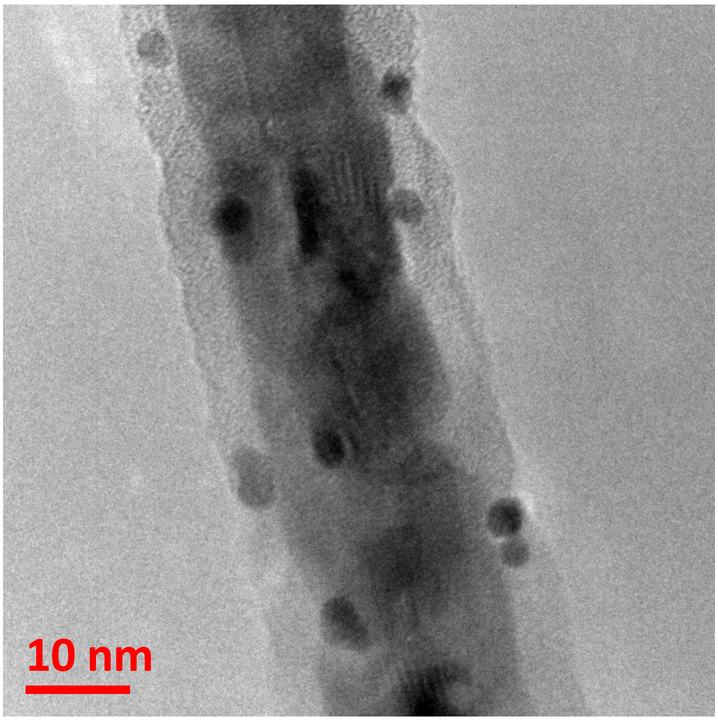

Figure S1. TEM image of Pt/CeO_2 nanotube@SiO_2 in a reducing gas environment such as hydrogen

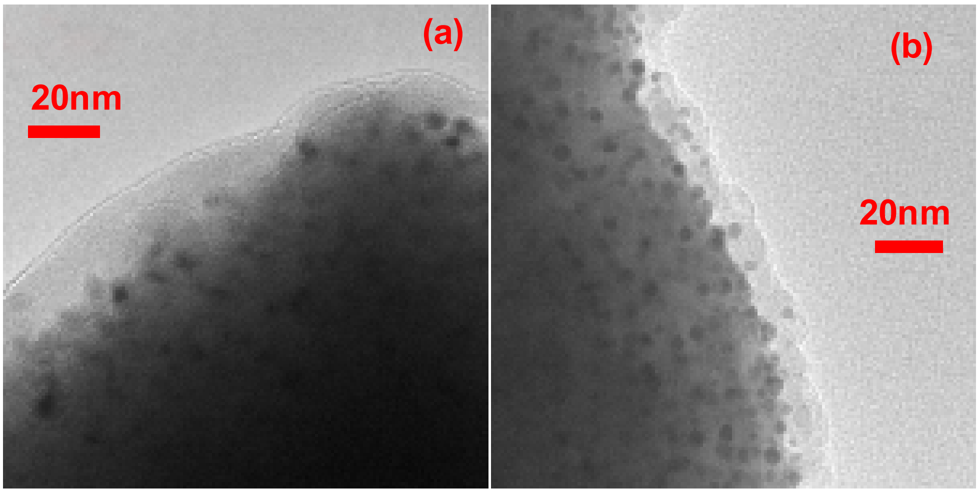

Figure S2. TEM images of Pt/CeO_2@SiO_2 calcined in air at (a) 500 °C for 2 h; (b) at 800 °C for 2 h

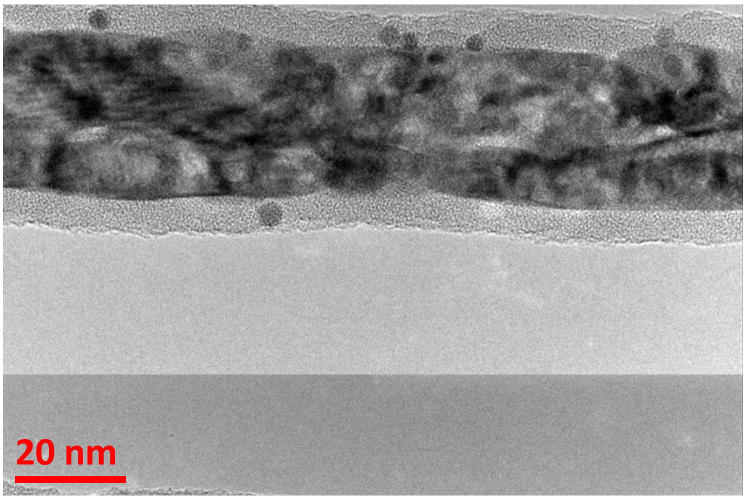

Figure S3. TEM image of the spent Pt/CeO_2 nanotube@SiO_2 catalyst