Supporting Information

The catalysts of self-assembled Pt@CeO_{2-δ}-rich core-shell nanoparticles on 3D ordered macroporous Ce_{1-x}Zr_xO₂ for soot oxidation: Nanostructure-dependent catalytic activity

Yuechang Wei,^a Jinqing Jiao,^a Xindong Zhang,^a Baofang Jin,^a Zhen Zhao*,^{a,b} Jing Xiong,^a Yazhao Li,^a Jian Liu,^a Jianmei Li ^a

^a State Key Laboratory of Heavy Oil Processing, College of Science, China University of Petroleum

^b Institute of Catalysis for Energy and Environment, Shenyang Normal University, Shenyang 110034, China

* Corresponding author: zhenzhao@cup.edu.cn; zhaozhen@synu.edu.cn

Postal Address: 18# Fuxue Road, Chang Ping District, Beijing, 102249, China,

Tel: 86-10-89731586, Fax: 86-10-69724721

1 Synthesis of materials

The self-assembly of Pt@CeO_{2-δ} core-shell nanoparticles on ordered macroporous Ce-based oxides is named as in situ colloidal crystal templates (CCT) method and the schematic representation is shown Figure S1. The processes of in situ CCT method in detail are presented as follows¹: Firstly, poly(methyl methacrylate) (PMMA) microspheres with non-crosslinking and monodispersion were synthesized by the modified emulsifier-free emulsion polymerization method with water-oil biphase double initiators. And the surface of PMMA microspheres exposes the polyelectrolyte brushes (PEBs, $[=NH_2]^+$ ·Cl⁻) which come from the initiators of 2, 2'-azobis (2-methylpropionamide) dihydrochloride (AIBA). Secondly, the dendritic platinum nanoparticles supported on the surface of PMMA microsphere were obtained by gas bubbling-assisted membrane reduction (GBMR) method with NaBH₄ as reduction agent. Thirdly, the CCT consisting of Pt/PMMA microspheres were filled by the solution of Ce(NO₃)₃·6H₂O and ZrOCl₂·8H₂O in ethylene glycol and methanol. Finally, the CCT were removed by calcinations, and the catalysts of 3DOM Ce_{1-x}Zr_xO₂-supported Pt@CeO_{2-δ} core-shell nanoparticles were one-pot synthesized.



Figure S1. Schematic representation of the preparation processing for self-assembly of $Pt@CeO_{2-\delta}$ core-shell nanoparticles on 3DOM $Ce_{1-x}Zr_xO_2$ support via in situ CCT method.

1.1 Synthesis of spherical PMMA accompanied with polyelectrolyte brushes (PEBs)

Non-crosslinked, monodispersed PMMA microspheres accompanied with PEBs ([=NH₂]⁺·Cl⁻) were synthesized using a modified emulsifier-free emulsion polymerization technique with water-oil biphase double initiators. The PEBs ([=NH₂]⁺·Cl⁻) came from the initiators of 2, 2'azobis (2-methylpropionamide) dihydrochloride (AIBA), and the preparation principles are showed in Figure S2. All water in the forthcoming synthetic steps was distilled and deionized to a resistivity of at least 12 M Ω ·cm. Methyl methacrylate (MMA, 80 ml) was refined through reduced pressure distillation. A four-necked, 1000 ml round-bottomed flask was filled with the mixture of acetone (50 ml) and water (150 ml), and then heated to 70 °C by a hot water bath, following the addition of the refined monomers. Attached to the flask was an electric motor driving a Teflon stirring paddle, a thermometer, a condenser, and a pipet through which nitrogen was bubbled to deaerate the mixture. AIBA (0.31 g, water phase initiator) and azodiisobutyronitrile (AIBN, 0.18 g, oil phase initiator) were added to 150 ml of water, and then were added to reactor when the water and monomers solution were heated to 70 °C. Under constant stirring (300 r/min) and with N₂ bubbling, the mixture was kept at 70 °C for 2 h. The resulting latex microspheres were filtered through glass wool to remove any large agglomerates. The PMMA microspheres accompanied with PEBs ([=NH₂]⁺·Cl⁻) were obtained.



Figure S2 The reaction equations for the synthesis of PMMA microspheres accompanied with PEBs ($[=NH2]+\cdot Cl$ -). Reaction (1) is the AIBA decomposition. Reaction (2) is the MMA polymerization under the action of the initiators.[1]

1.2 Synthesis of PMMA-supported dendritic platinum nanoparticle complex

The PMMA-supported dendritic platinum nanoparticles (DPNPs) complex was synthesized by GBMR method with NaBH₄ as reduction agent. The schematic diagram of preparation method is presented in Figure S3. The typical preparative procedures are described as follows: The 250 ml of PMMA latex (average size of 350 nm, solid content ~10 wt %) was placed in a precursor tank, then the H₂PtCl₆ solution was added slowly to the microspheres latex under stirring conditions. The PEBs ($[=NH_2]^+$ ·Cl⁻) on the surface of PMMA microspheres can interact with the anions of $[PtCl_6]^2$. The mixture solution was driven by a peristaltic pump at ~360 ml min⁻¹ flow rate to form a tubal cycling flow. A reductant solution (NaBH₄) (50 ml) was injected to the membrane reactor with two ceramic membrane tubes (Φ 3 mm \times 160 mm) by a constant flow pump at flow rate of 1 ml min⁻¹. Meantime, the hydrogen gas was also injected by the two other membrane tubes. The metal precursor solution flowed in the glass tube reactor and outside the ceramic tubes. The NaBH₄ solution was infiltrated through the abundant holes (d=40 nm) on the wall of the ceramic tubes into the glass tube reactor, where the reduction of metal ions occurred immediately when the two solutions met. The molar ratio of $[PtCl_6]^{2-}$ to NaBH₄ was about 1:5. The $[PtCl_6]^{2-}$ ions on the surface of microspheres were reduced by NaBH₄. The color of the mixture changes from lacte to incanus. The hydrogen bubbling-assisted stirring operation (10 ml min⁻¹) was developed to vigorously stir the solution and to make the reaction homogenous. The synthesis process was stopped after complete consumption of the NaBH₄ solution. The dendritic Pt nanoparticles were obtained and stabilized on the surface of PMMA and they are generically named as Pt/PMMA complexes. Finally, Pt/PMMA complexes with dendritic Pt nanoparticles were centrifuged at 3000 r/min for 10 h to form CCT and the complexes were dried in air at room temperature.



Figure S3 Schematic representation for the synthesis of dendritic platinum nanoparticles (DPNPs) on the surface of PMMA microsphere by GBMR method.[1]

1.3 Synthesis of 3DOM $Ce_{1-x}Zr_xO_2$ -supported $Pt@CeO_{2-\delta}$ core-shell nanoparticle catalysts

3DOM Ce_{1-x}Zr_xO₂-supported Pt@CeO_{2-δ} core-shell nanoparticle catalysts were synthesized by in situ CCT method. The ethylene glycol (EG)-methanol solution of Ce(NO₃)₃·6H₂O and ZrOCl₂·8H₂O (the volume ratio of 3:2) as precursors were added to the CCT, and permeated the voids between the close-packed spheres. Excessive liquid was removed from the impregnated microspheres template via a Buchner funnel connected to vacuum. The infiltered template was allowed to dry in drying oven at 50 °C for 24 h. Finally, the dried sample was mixed with quartz sand (10-15 mesh) followed by heating in a quartz tube at the rate of 1 °C /min from room temperature to 550 °C in air for 4 h to remove the CCT, and then 3DOM Ce_{1-x}Zr_xO₂-supported platinum catalysts were obtained. The catalysts will be generically named as 3DOM Pt@CeO_{2-δ}/ Ce_{1-x}Zr_xO₂. In order to contrast the structural characteristics of Pt@CeO_{2-δ} core-shell nanoparticle, 3DOM Ce_{1-x}Zr_xO₂-supported bare Pt nanoparticles named as 3DOM Pt/Ce_{1-x}Zr_xO₂ catalyst was also synthesized by GBMR method.



Figure S4 TEM image of model soot particles.



Figure S5 TEM and HRTEM images of 3DOM Pt/Ce_{0.8}Zr_{0.2}O₂ catalyst.



Figure S6 TEM (A) and HRTEM (B) images of 3DOM $Pt/Ce_{0.2}Zr_{0.8}O_2$ catalyst synthesized by

GBMR method.



Figure S7 Pore size distribution of 3DOM Pt@CeO_{2- δ}/Ce_{1-x}Zr_xO₂ catalysts determined by mercury intrusion porosimetry (MIP). a. Pt@CeO_{2- δ}/Ce_{0.8}Zr_{0.2}O₂; b. Pt@CeO_{2- δ}/Ce_{0.6}Zr_{0.4}O₂; c. Pt@CeO_{2- δ}/Ce_{0.2}Zr_{0.8}O₂; d. Pt/ZrO₂



Figure S8 XRD patterns of 3DOM Pt@CeO_{2- δ}/Ce_{0.8}Zr_{0.2}O₂ catalyst obtained at different calcination temperatures (550 and 650 °C) for 4h.

| 3DOM Catalysts | T ₁₀ (°C) | T ₅₀ (°C) | T ₉₀ (°C) | S _{CO2} ^m (%) |
|-----------------------|----------------------|----------------------|----------------------|-----------------------------------|
| CeO ₂ | 411 | 492 | 513 | 89.5 |
| $Ce_{0.8}Zr_{0.2}O_2$ | 409 | 488 | 512 | 86.6 |
| $Ce_{0.6}Zr_{0.2}O_2$ | 432 | 510 | 541 | 86.3 |
| $Ce_{0.4}Zr_{0.6}O_2$ | 443 | 541 | 579 | 82.0 |
| $Ce_{0.2}Zr_{0.8}O_2$ | 486 | 563 | 592 | 71.2 |
| ZrO ₂ | 493 | 593 | 649 | 63.6 |

Table S1 The catalytic activity of 3DOM $Ce_{1-x}Zr_xO_2$ catalysts obtained by GBMR method for soot oxidation under the condition of loose contact in the presence of O_2 .

Reaction rate at 300 °C, 5 % O2 in Ar, 50 ml min-1

 T_{10} T₅₀ T₉₀ $S_{CO2}{}^{m}$ Catalysts (^{o}C) $(^{\circ}C)$ $(^{\circ}C)$ (%) Pt/CeO₂-GBMR 341 420 465 97.9 Pt/Ce_{0.8}Zr_{0.2}O₂-GBMR 326 418 462 97.6 Pt/Ce_{0.6}Zr_{0.2}O₂-GBMR 352 439 478 96.8 Pt/Ce_{0.4}Zr_{0.6}O₂-GBMR 97.0 361 466 505 Pt/Ce_{0.2}Zr_{0.8}O₂-GBMR 396 482 527 92.6

Table S2 The catalytic activity of 3DOM $Pt/Ce_{1-x}Zr_xO_2$ catalysts obtained by GBMR method for soot oxidation under the condition of loose contact in the presence of O_2 .

Reaction rate at 300 °C, 5 % O₂ in Ar, 50 ml min⁻¹

(1) Y. Wei, Z. Zhao, J. Liu, C. Xu, G. Jiang, A. Duan, Small. 2013, 9, 3957-3963.