High efficient catalysts of ordered macroporous Ce$_{1-x}$Zr$_x$O$_2$-supported Pt@CeO$_2$& core-shell nanoparticles for soot oxidation

Yuechang Wei, Zhen Zhao*, Jian Liu, Guiyuan Jiang, Aijun Duan
State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, (China)
*corresponding author: zhenzhao@cup.edu.cn

Introduction
Soot particle emitted from diesel engine vehicles is one of probable precursors to dangerous for human health. Development of catalysts, which decrease the emission amount of diesel soot, is one of the focus research topics in the field of environmental catalysis. 3DOM Ce-based oxide catalysts have been demonstrated as good candidate catalysts or supports for diesel soot combustion due to their good redox properties and big pore sizes. However, the catalytic performance is limited by the intrinsic activity of metal oxide. Noble metals acting as an active site supported on the surface of oxides can modify the intrinsic catalytic properties of themselves. Among the reported catalysts for soot oxidation, Pt-based catalysts are still the best catalytic system, and are also currently commercialized for practical conditions. The catalytic performance of Pt nanocrystals can be finely tuned by their shape. Thus, the shape-controlled synthesis of Pt@CeO$_2$ core-shell nanoparticles over 3DOM Ce$_{1-x}$Zr$_x$O$_2$ support is a potential route for enhancing their catalytic activities.

Materials and Methods
3DOM Ce$_{1-x}$Zr$_x$O$_2$-supported Pt@CeO$_2$ core-shell nanoparticle (NPs) catalysts were synthesized by in situ colloidal crystal templates (CCT) method. The synthetic method of Pt@CeO$_2$ NPs supported on 3DOM Ce$_{1-x}$Zr$_x$O$_2$ support involves three processes as following.

Firstly, Non-crosslinked, monodisperse PMMA microspheres accompanied with polyelectrolyte brushes ([=NH$_2$]$^\text{-}$-Cl) were synthesized using a modified emulsifier-free emulsion polymerization technique with water-oil biphase double initiators.

Secondly, the PMMA with polyelectrolyte brushes ([=NH$_2$]$^\text{-}$-Cl)-supported platinum nanoparticles were synthesized by the membrane-diffused reduction method with NaBH$_4$ as reduction agent. The polyelectrolyte brushes ([=NH$_2$]$^\text{-}$-Cl) on the surface of PMMA microspheres can interact with the anions of [PtCl$_6$]$^2^-$. The PtCl$_6$ ions on the surface of microspheres were reduced by reduction agent (NaBH$_4$). The platinum nanoparticles were obtained and stabilized on the surface of SPBs. Then, the SPBs-supported GNP complexes were centrifuged to form CCT and the complexes were dried in air at room temperature.

Thirdly, a series of 3DOM Ce$_{1-x}$Zr$_x$O$_2$-supported Pt@CeO$_2$ NPs catalysts were prepared using ethylene glycol (EG)-methanol solution of Ce(NO$_3$)$_3$·6H$_2$O and ZrOCl$_2$·8H$_2$O as precursors. The precursors were added to the CCT. Finally, the dried sample was heated to remove the CCT, and then the catalysts were obtained.

Results and Discussion
Fig. 1a shows the typical SEM images of CCT assembled using Pt/PMMA microspheres. It can be seen that the average size of the monodisperse PMMA microspheres is about 350 nm. A face-centered-cubic (fcc) array of spheres with facets corresponding to the (111) sets of planes can be clearly observed from the image. As shown in Fig. 1b, well-defined metallic Pt nanoparticles have been obtained for [Pt]/[PMMA] used herein. The Pt nanoparticles were nearly 100% in nanodendrite shape. Fig. 1c gives the HRTEM image of a single Pt nanodendrite, which clearly shows overgrowth of Pt branches on the PMMA microsphere.

HRTEM images of individual Pt branches (Fig. 1d) show their single crystalline structure with a highly ordered continuous fringe pattern. The presence of single crystal Pt branches will improve the contact area between Pt nanocrystal and the precursor of 3DOM oxides, which could be about to produce unexpected nanostructure for the next synthesized step. Fig. 1e shows SEM image of Pt@CeO$_2$/Ce$_{1-x}$Zr$_x$O$_2$ catalysts synthesized by in situ CCT method. The SEM image exhibits that the macroporous material contains a skeleton surrounding uniform close-packed periodic voids with the average diameter of 260±10 nm. The wall thicknesses observed from SEM images are 30±5 nm, illustrates that the wall is composed of crystallite grains. The next layer is highly visible in the inset of SEM image and the voids are interconnected through the open window, ca. 80±5 nm in diameter.

Acknowledgement
We acknowledge the financial supports from the National Natural Science Foundation of China (No. 21171681, 21303263 and 21173270) and Science Foundation of China University of Petroleum, Beijing (No. 2462013YJRCC13 and 2462013BBRC003).

References
2. Y. Wei, Z. Zhao, J. Liu, et al., Small, 2013, 9, 3957.