How Pt Interacts with CeO_2 under the Reducing and Oxidizing Environments at Elevated Temperature? The Origin of Improved Thermal Stability of Pt/CeO_2 Compared to CeO_2

Jaeha Lee[1], YoungSeok Ryou[1], Xiaojun Chan[2], Tae Jin Kim[2], Do Heui Kim[1]*

[1]School of Chem. and Bio.Eng., Seoul National University, Seoul, 151-744 Rep. of Korea
[2] Department of Mat. Sci. and Chem. Eng., Stony Brook University, Stony Brook, NY 11794, USA
**corresponding author:dohkim@snu.ac.kr*

Introduction

Higher metal dispersion can be obtained via strong interaction between metal and support. Nagai et al. reported that Pt-Ceria interaction maintains high platinum dispersion even after oxidative treatment at high temperature based on the EXAFS spectroscopy results, which demonstrated the formation of strong Pt-O-Ce bond.[1] Farmer and Campbell also reported that Ceria maintains small metal particle size through strong metal support interaction.[2] Many catalytic reactions, including automotive catalytic reaction and water-gas-shift reaction, utilize such strong metal support interaction between precious metal and Ceria to attain high catalytic activity. Therefore, understanding metal-Ceria interaction is of practical importance to provide rational design of Ceria based catalysts.

In the present work, Pt-Ceria interaction under the oxidizing/reducing environment and the role of the interaction in determining the thermal stability of Pt/CeO_2 were investigated in detail. It was found that Pt-O-Ce bond formed upon oxidative treatment plays a crucial role in preventing Ceria agglomeration at elevated temperature.

Materials and Methods

Ceria, obtained from Rhodia, had a surface area of 120 m^2/g. 2 wt% of Pt was impregnated on Ceria by the incipient wetness impregnation method with aqueous $Pt(NH_3)_4(NO_3)_2$ (Sigma Aldrich, 99.99 % grade, metal basis) solution. Dried samples were treated in flowing 100 mL/min of 15 $\%O_2/N_2$ or 10 $\%H_2/N_2$ or N_2 for 2 h at the selected temperature; capital letter C, R, and NC represent each treatment, respectively. For example, $Pt(2)/CeO_2$ 500C 250R 800NC was prepared by oxidizing $Pt(2)/CeO_2$ sample at 500 ºC for 2 h, followed by reducing at 250 ºC for 2 h, and then thermally treating under N_2 flow for 2 h.

Pt-Ceria interaction has been extensively investigated by combining various characterization methods including X-ray diffraction (XRD), N_2 adsorption/desorption (BET/BJH), H_2 temperature programmed reduction (TPR), pulsed and static CO-chemisorption, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and Raman spectroscopy.

Results and Discussion

According to Raman spectroscopy, Pt/CeO_2 possesses strong Pt-O-Ce bond after the oxidative treatment. After the reductive treatment at mild temperature (< 500 ºC), Pt seems to situate on the oxygen vacancy of Ceria surface, based on CO chemisorption results. At reduction temperature of 800 ºC, where bulk Ceria is reduced, the structure of Pt/Ceria collapsed.

Under the oxidative atmosphere, it was observed that the strong Pt-O-Ce bond maintains ceria structure from collapsing even at high temperature as high as 800 ºC. When Pt-O-Ce bond was selectively removed, thermal stability of Pt/Ceria was greatly weakened. **Figure 1(a)** is H_2-TPR curve of $Pt(2)/CeO_2$ 500C catalyst. Two reduction peaks centered at ~100 ºC and ~780 ºC are observed; the former originates from the reduction of Pt-O-Ce bond and surface Ceria while the latter originates from the reduction of bulk Ceria. By reducing the catalyst at 250 ºC, Pt-O-Ce bond can be eliminated completely without affecting the pore structure of Ceria. **Figure 1(b)** is BJH pore size distribution curve of $Pt(2)/CeO_2$ catalyst after different thermal treatments (500C, 500C 250R 800NC, and 500C 800NC). $Pt(2)/CeO_2$ was treated at 800 ºC under the N_2 flow (inert gas), with and without Pt-O-Ce bond. On **Figure 1(b)**, it is observed that in the presence of Pt-O-Ce bond the pore structure of $Pt(2)/CeO_2$ was maintained (800C and 500C 800NC), while in the absence of Pt-O-Ce bond the pore structure collapsed significantly (500C 250R 800NC). This strongly implies that the presence of Pt-O-Ce bond is crucial to prevent Ceria agglomeration at high temperature under the oxidative atmosphere. It was confirmed that the thermal stability of Ceria is enhanced in the presence of Pt-O-Ce bond.

While Pt-O-Ce bond inhibited Pt sintering and Ceria agglomeration, Pt-Ceria interaction was strengthened after the oxidative treatment at high temperature. To explain the phenomena, Pt-diffusion model is proposed, based on H_2-TPR, In-situ Raman, and XPS results.

Significance

Strong Pt-O-Ce bond inhibits Pt sintering as well as Ceria agglomeration even at temperature as high as 800 ºC. Thermally stable catalyst could be rationally designed and developed by utilizing such strong Pt-Ceria interaction.

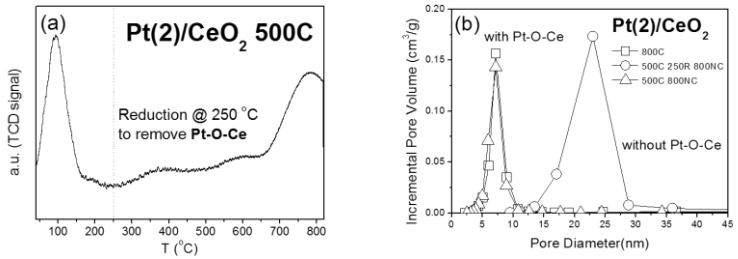

Figure 1. (a) H_2-TPR curve of $Pt(2)/CeO_2$ 500C. Reductive treatment at 250 ºC reduces Ceria surface as well as Pt-O-Ce bond. (b) BJH pore size distribution curve of $Pt(2)/CeO_2$ catalyst, after various thermal treatments (800C, 500C 250R 800NC, 500C 800NC).

References

1. Y. Nagai et al., *J. Catal.*, 242 103–109 (2006).
2. J.A. Farmer, C.T. Campbell *Science*, 329, 5994, 933-936 (2010).
3. J.H. Lee et al, *J. Phys. Chem. C*, **DOI:** 10.1021/acs.jpcc.6b08656.