

# Nano CeO<sub>2</sub>-ZrO<sub>2</sub>/mesoporous silica composite materials with higher oxygen storage capacity and improved CO oxidation efficiency

K. K. Cheralathan<sup>1</sup>, K. Nakamura<sup>1</sup>, H. Hirata<sup>2</sup>, and M. Ogura<sup>1\*</sup>

<sup>1</sup> Institute of Industrial Science, The University of Tokyo, Tokyo 153-8505 (Japan)

<sup>2</sup> Toyota Motor Corporation, Higashifuji Technical Center, Susono, Shizuoka 410-1193 (Japan)

\*oguram@iis.u-tokyo.ac.jp

## Introduction

Mesoporous CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxide with large surface area, narrow pore size distribution and high thermal stability would be advantageous for improving the performance of automobile three-way catalytic systems. Direct synthesis methods were employed for the preparation of mesoporous CeO<sub>2</sub>-ZrO<sub>2</sub> [1]. However, collapse of the mesostructure of these materials is often resulted at high temperature operations due to sintering. Keeping this in mind, we intend to prepare SBA-15 mesoporous silica coated with CeO<sub>2</sub>-ZrO<sub>2</sub> nanolayer or nano particles on the mesopore walls, expecting that the thermally stable silica backbone and mesopores of SBA-15 would provide high thermal stability to the anchored CeO<sub>2</sub>-ZrO<sub>2</sub> nanolayer or nanoparticles. Further we aim that these composite materials would behave like mesoporous CeO<sub>2</sub>-ZrO<sub>2</sub> and perform better than bulk CeO<sub>2</sub>-ZrO<sub>2</sub> in terms of oxygen storage capacity (OSC) and CO oxidation activity since loading CeO<sub>2</sub>-ZrO<sub>2</sub> into mesopores improves porosity and increases surface area of the guest phase. Recently we have developed a novel method named vapour-induced internal hydrolysis (VIH) to coat large quantities of ZrO<sub>2</sub> on the mesopore walls of SBA-15 without any pore blocking [2]. In order to coat CeO<sub>2</sub>-ZrO<sub>2</sub> on the pore walls of SBA-15, we extended the similar methodology.

## Materials and Methods

SBA-15 was prepared by following the procedure reported elsewhere [3]. The precursors, (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> or Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O of CeO<sub>2</sub> and ZrO<sub>2</sub> respectively, were dissolved in water and wet impregnated into the mesopores of SBA-15. The resulted precursor loaded material was treated in an autoclave with NH<sub>3</sub>/H<sub>2</sub>O vapours at predetermined temperature and time under autogenously generated pressure to facilitate internal hydrolysis of the precursors. After this VIH step, the samples were dried and then calcined at 500°C in air. The loading of CeO<sub>2</sub>-ZrO<sub>2</sub> was 36 wt%. A sample of SBA-15, first coated with 24 wt% ZrO<sub>2</sub> and then loaded with 36 wt % CeO<sub>2</sub>-ZrO<sub>2</sub> was also prepared. Pt (0.1 wt%) was loaded on the prepared samples by using H<sub>2</sub>PtCl<sub>6</sub> as the source of Pt. The obtained materials were characterized by N<sub>2</sub>-sorption, X-ray diffraction, TEM and H<sub>2</sub>-TPR analysis. CO oxidation was used as a tool to evaluate the catalytic activity.

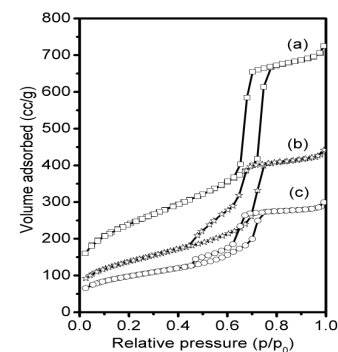
## Results and Discussion

Nitrogen sorption analysis (Figure 1.) of CeO<sub>2</sub>-ZrO<sub>2</sub> loaded SBA-15 samples prepared by VIH method (36-CeZr-100-5h) and conventional wet impregnation method (36-CeZr-DC) indicated the existence of metal oxide particles inside the nanopores. Wide angle XRD patterns of the samples showed the presence of nanosized CeO<sub>2</sub> layer or particles and amorphous ZrO<sub>2</sub> instead of CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution phase. The broadening of the XRD patterns and their decreasing peak intensities together with N<sub>2</sub> sorption data revealed that VIH improved the dispersion of CeO<sub>2</sub> inside the pores of SBA-15. TEM images showed the intactness of the mesoporous structure and EDS analysis indicated uniformity

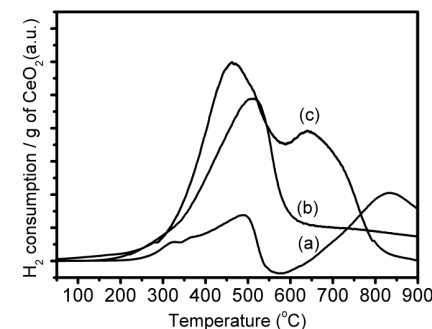
of the CeO<sub>2</sub>-ZrO<sub>2</sub> distribution. The amount of consumed H<sub>2</sub> (Figure 2.) revealed that OSC of the CeO<sub>2</sub>-ZrO<sub>2</sub> coated SBA-15 sample was better than that of bulk-CeO<sub>2</sub>-ZrO<sub>2</sub> and bulk-CeO<sub>2</sub>. Among CeO<sub>2</sub>-ZrO<sub>2</sub> coated, and first ZrO<sub>2</sub> coated and then CeO<sub>2</sub>-ZrO<sub>2</sub> coated SBA-15 materials sintered at 950°C, the latter showed presence of nano-sized, single phase CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution. This solid solution sample possessed lesser OSC compared to its unsintered counterpart but it better retained its OSC during repeated redox cycles. CO oxidation experiments revealed that Pt-loaded CeO<sub>2</sub>-ZrO<sub>2</sub>-coated SBA-15 samples catalyze CO oxidation at lower temperatures compared to Pt loaded bulk-CeO<sub>2</sub>-ZrO<sub>2</sub> and bulk-CeO<sub>2</sub> samples, which is proving the superiority of the novel CeO<sub>2</sub>-ZrO<sub>2</sub>/SBA-15 composite materials.

## Significance

CeO<sub>2</sub>-ZrO<sub>2</sub> is an important component of three-way catalyst systems used in automobile exhaust pipes for pollution abatement. Improving its porous properties and catalytic performance would help to make more efficient catalytic converters that will cope up with ever increasing stringent eco regulations.



**Figure 1.** N<sub>2</sub> sorption isotherms of (a) SBA-15, (b) 36-CeZr-DC and (c) 36-CeZr-100-5h.



**Figure 2.** H<sub>2</sub> – TPR profiles of (a) bulk-CeO<sub>2</sub> (b) bulk-Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> and (c) 36-CeZr-100-5h.

## References

1. Yuan, Q., Liu, Q., Song, W.-G., Feng, W., Pu, W.-L., Sun, L.-D., Zhang, Y.-W., Yan, C.-H. *J. Am. Chem. Soc.* 129, 6699 (2007).
2. Cheralathan, K. K., Hayashi, T., Ogura, M. *Adv. Mater.* 20, 2131 (2008).
3. Zhao, D., Feng, J., Huo, Q., Melosh, N., Fredrickson, G. H., Chmelka, B. F., Stucky, G. D. *Science* 279, 548 (1998).