Monolithically integrated metal oxide nano-arrays as cost-effective and high performance oxidation catalyst

Zheng Ren[1], Yanbing Guo[1], Sibo Wang[1] and Pu-Xian Gao[1*]
[1]*Department of Materials Science and Engineering & Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3136*
**corresponding author:puxian.gao@ims.uconn.edu*

Introduction

Discovery and design of cost-effective, efficient, and multifunctional heterogeneous catalysts are significant for chemical industry. Monolithic devices, such as catalytic converters, filters, and reactors, are generally more efficient and cost- effective compared with powder or pellet counterparts resulting from several advantageous features including low pressure drop, high geometric surface area and efficient mass transfer. However, three main issues remain challenging for the development of monolithic catalytic devices: i) The inevitable use of precious metals (Pt, Rh, and Pd) makes it expensive with limited materials supply; ii) Empirical wash-coated powder-form catalysts lack the well-defined structural and geometrical configurations, which compromises the catalytic performance and materials utilization efficiency; iii) Current understanding of the relationship between practical industrial catalysts' performance and the origin of catalytic activity is quite limited. Here we present a low temperature solution based method for monolithic integration of nanowires onto commercial cordierite honeycombs. Various 3D nanoarrays have been developed and their performance towards low temperature oxidation of CO and NO has been investigated.

Materials and Methods

We directly grow three-dimensional ZnO, TiO_2, CeO_2 and Co_3O_4 nanowire arrays onto the cordierite honeycombs with or without colloidal deposition of Pt nanoparticles. The low temperature CO oxidation and hydrocarbon combustion were investigated by using BenchCAT reactor connected to micro-GC. The NO oxidation test was conducted by FT-IR spectrometer. The space velocity of all the catalyst tests was controlled to be ~45,000/h and about 0.1g monolithic catalyst was used.

Results and Discussion

The catalytic performance can be tuned by varying the nanostructure's geometry. By replacing the traditional wash-coated catalytic layers with nanowire arrays, we have reduced the noble metal and support materials usage by 10-40 times without sacrificing the catalytic performance. Meanwhile the nano-array based catalytic honeycombs demonstrate good robustness under high temperature and fast gas flows. Figure 1demonstrates the CO oxidation performance, a probe reaction to compare the materials utilization efficiency without sacrificing the catalytic activity. Meanwhile, by tuning the nanoscale geometry the catalytic performance could be adjusted respectively as shown in Figure 1 where ZnO nanostructures of different morphology were used as the support for Pt nanoparticles.

Much research effort has been further focused on Co_3O_4 nanowire arrays due to its catalytic activity towards multiple chemical reactions. The high efficient nitric oxide oxidation (80% NO to NO_2 conversion) has been achieved under temperature as low as 275 °C, which is of great importance to NO_x removal technologies such as selective catalytic reduction (SCR) and NO_x storage and reduction (NSR). Furthermore, we have successfully achieved a large scale production of Co_3O_4 and cobaltite nanowire arrays on commercial cordierite honeycombs of 3cm×4cm in cross section and 5 cm in channel length. The cobalt oxide based nanowire arrays displayed good catalytic performance towards multiple reactions such as carbon monoxide, and nitric oxide oxidation. Figure 2 demonstrates the scale up process of Co_3O_4 nanoarray monolithic catalyst and their performance towards NO oxidation. The high catalytic activity could be ascribed to the enhanced surface area by the nanostructure deposition. The gas solid interaction is believed to be greatly facilitated owing to the ordered arrangement of nanowire arrays.

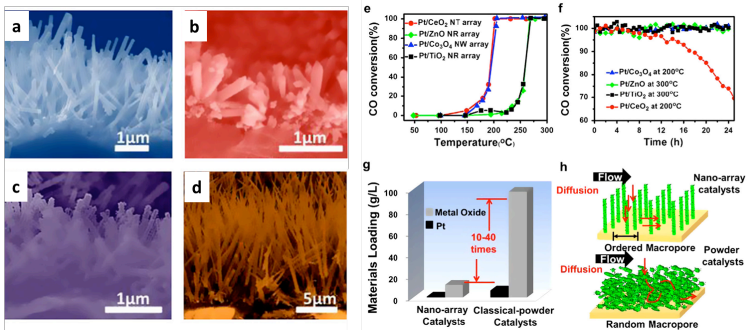

Figure 1. a-d) Nanoarray catalyst of ZnO, TiO_2, CeO_2 and Co_3O_4; e-f) CO oxidation performance of nanoarray catalyst with Pt decoration; g-h) comparison of the materials usage and gas solid interaction of nanowire array and powder catalyst.

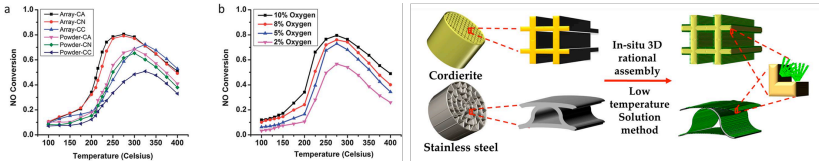

Figure 2. a-b) Low temperature NO oxidation of Co_3O_4 nanoarray; c) Scale up process of Co_3O_4 nanoarray on large scale honeycombs.

Significance

Substitution of washcoated nanopowder catalyst with ordered nanoarray catalyst by hydrothermal growth enables low-cost design and processing of catalyst preparation and enhances the materials utilization efficiency without sacrificing the catalytic performance.

References

[1] Guo and Ren et. al, *Nano Energy*, 2013,2, 873–881
[2] Ren et. al, *J. Mater. Chem. A* , 2013, 1, 9897-9906.