



# Nano-array based monolithic catalysts: Concept, rational materials design and tunable catalytic performance



Zheng Ren, Yanbing Guo, Pu-Xian Gao\*

Department of Materials Science and Engineering & Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3136, USA

## ARTICLE INFO

### Article history:

Received 1 November 2014

Received in revised form 5 January 2015

Accepted 28 January 2015

Available online 21 March 2015

### Keywords:

Monolithic catalyst

Nano-arrays

Rational materials design

Scalable synthesis

Structure–property relations

Low temperature oxidation

## ABSTRACT

Monolithic catalysts, also known as structured catalysts, represent an important catalyst configuration widely used in automotive, chemical, and energy industries. However, several issues associated with washcoat based monolithic catalyst preparation are ever present, such as compromised materials utilization efficiency due to a less-than-ideal wash coating process, difficulty in precise and optimum microstructure control and lack of structure–property correlation. In this mini-review, we introduce the concept of nano-array catalyst, a new type of monolithic catalyst featuring high catalyst utilization efficiency, good thermal/mechanical robustness, and catalytic performance tunability. A comprehensive overview is presented with detailed discussion of the strategies for nano-array catalyst preparation and rational catalytic activity adjustment enabled by the well-defined nano-array geometry. Specifically their scalable fabrication processes are reviewed in conjunction with discussion of their various catalytic oxidation reaction performances at low temperature. We hope this review will serve as a timely and useful research guide for rational design and utilization of the new type of monolithic catalysts.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Monolith structure represents an important configuration of reactors in many applications such as fine chemical processing, environmental catalysis and clean energy combustion [1–9]. The monolith structure can be made by various types of materials such as metals, ceramics, and polymers. Amongst them, ceramic monolith made of cordierite ( $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ ) is one of the major types of monoliths used as catalytic reactors for automotive emission control [3,10–12], diesel particulate filter (DPF) [13–15], indoor air purification [16] and water filtration [17–19] due to its low thermal expansion coefficient, high thermal shock resistance, relatively high porosity, low weight but good mechanical durability [3,20]. Fig. 1 shows a photograph of cordierite ceramic monolith purchased from Corning Incorporated. The cordierite monolith consists of parallel channels that extend throughout the substrate. The geometric characteristics of this ceramic monolith are described by several parameters including cell density, hydraulic diameter, wall thickness and open frontal area. If the cell spacing  $L$  is defined as the distance between the centers of adjacent channels, the hydraulic diameter is thus  $D=L-t$  where  $t$  represents the wall thickness. The cell density  $N=1/L^2$  is defined as the number of cells per unit

cross-sectional area. The open frontal area  $\text{OFA}=(L-t)^2/L^2=D^2N$  is the fraction of the open cross-sectional region in an individual cell. The monolith configuration and the ceramic cordierite enable several advantages in gas phase reactions especially in automotive emission control. The high thermal shock resistance and sufficient mechanical strength allow it to survive under various automotive operation conditions. Furthermore, the low pressure drop to surface area ratio enabled by high cell density and large OFA is beneficial to handle large flow rate with less energy consumption which successfully reduce the cost of exhaust after-treatment. The large OFA also favors the treatment of stream with particulate and dust for DPF application to remove soot particles in diesel engines.

Despite all the benefits the monolith configuration is able to provide, challenges remain for preparation of monolithic catalysts. Typically the catalyst preparation requires a uniform coating upon the monolithic substrate of either ready-made catalysts (e.g. zeolites) which do not need specific catalytic supports or both support and catalytic active materials [21]. For example, wash-coating of  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2$  or carbon as the catalyst support is usually the first step of the monolithic catalyst fabrication followed by the dispersion of active noble metal (Pt, Rh or Pd) nanoparticles. Two typical strategies, pore-filling and slip-casting, are widely used for this wash coating procedure. The pore filling refers to the filling of pores in the monolith ceramics with support materials by colloidal coating which features strong interaction between the support and the substrate. Although mono-dispersed  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  colloidal

\* Corresponding author. Tel.: +1 8604869213.

E-mail address: [puxian.gao@ims.uconn.edu](mailto:puxian.gao@ims.uconn.edu) (P.-X. Gao).

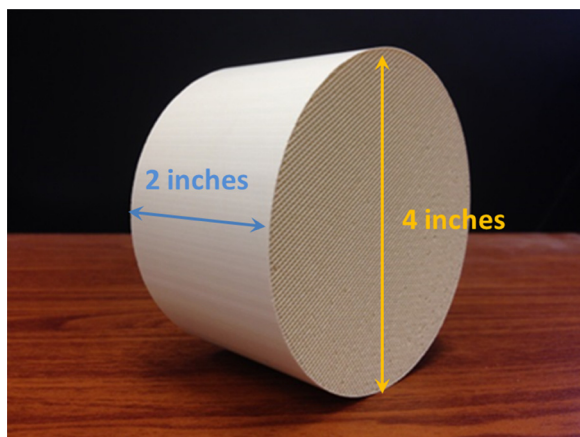


Fig. 1. A photograph of a cordierite monolith purchased from Corning Incorporated.

suspension is easily to be prepared by wet chemical synthesis and the pore-filling process ensures the good adherence since the support materials is confined in the pores, the loading amount is very limited given the relatively small pore volume and low surface area of the cordierite monolith [3]. The slip-casting strategy, also known as slurry coating, is usually employed to increase the materials loading. Since the layer is thicker and most of the materials are not confined to the pores, the adherence to the monolith must be enhanced by adding binders. Such slurry coating sacrifices the catalyst utilization efficiency as a consequence of large amount of catalyst loading. It also adds complexity to the materials processing by the addition of binders because the viscosity of the slurry needs to be carefully controlled and any wrongly prepared slurry precursor will lead to poor adherence to the substrate. In addition, a number of repeated coating procedures are often required to ensure a uniform coverage. Therefore the traditional monolithic catalyst configuration faces several challenges. Firstly, the significant amount of materials loading imposes great pressure on the noble metal supply which makes the catalytic converters rather expensive for automotive emission control. Secondly, the less-than-ideal wash-coating process usually does not ensure uniform catalyst deposition with precisely and optimally controlled microstructures, therefore compromises the materials utilization efficiency. Lastly, the random structural arrangement of the wash-coated materials renders difficulty to well correlate catalyst structure, porosity, orientation and the relevant gas–solid interactions with catalyst performance and it is thus no easy task for the rational catalyst design.

To meet the above challenges of traditional wash-coat based monolithic catalysts, in the past few years, a distinct monolithic catalyst configuration, nanostructure array (nano-array) based monolithic catalysts, has been invented and demonstrated in our research group by in situ growing hierarchically arranged arrays of various types of nanostructures such as nanowires, nanorods and nanotubes onto bare channeled monolithic substrates [22–24]. The unique in situ solution based self-assembly and integration process and ordered nano-arrays instead of wash-coated catalyst layers on the three-dimensional (3D) monolith substrate differentiate the nano-array catalyst from the traditional monolithic catalyst in terms of fabrication and structural characteristics. Furthermore, the well-defined structural and chemical characteristics conveyed by this new type of structured catalysts have demonstrated potential figures of merits in excellent robustness, high materials utilization efficiency, as well as tunable catalytic functions toward various gas phase reactions at low temperature. The gas phase reactions include CO oxidation, hydrocarbon oxidation, as well as nitric oxide oxidation and reduction. In this article, this new concept of

nano-array based monolithic catalysts will be introduced with their latest research progress comprehensively reviewed. Specifically, our discussion will be focused on reviewing the progress on the rational catalyst materials design and preparation, and highlighting the demonstrated figures of merit in high robustness, materials utilization efficiency and tunable catalytic reaction activity toward various catalytic oxidations at low temperature.

## 2. Concept of nano-array based monolithic catalysts

The typical structural configuration of nano-array based monolithic catalysts is illustrated in Fig. 2, where nano-arrays such as nanowire arrays are distributed uniformly on the channel surfaces of cordierite monolith [22]. The nano-arrays can either act as the support for catalytic active materials or function as the catalysts themselves. The height of nanowire arrays is usually less than  $10\ \mu\text{m}$ , much thinner than the wash-coat thickness ( $\sim 40\text{--}100\ \mu\text{m}$ ) in traditional wash-coated structured catalysts, thus greatly improve the catalyst utilization efficiency by enabled shorter diffusion distance and low materials usage. The mass loading of these nano-arrays only constitutes 5–15% of the monolithic catalyst. Using CO oxidation as the probe reaction we have discovered the nano-array configuration reduces the materials utilization by an order of magnitude without sacrificing the catalytic activity. For example, 1% Pt supported on ZnO nano-arrays ( $\sim 0.1\ \text{mg Pt}$  and  $\sim 10.0\ \text{mg ZnO}$ ) is able to achieve complete CO oxidation below  $300\ ^\circ\text{C}$  at a relatively large space velocity of  $\sim 50,000\ \text{h}^{-1}$ .

Other advantageous features of nano-array catalyst over wash-coated particulate form catalyst include the high surface area, thermal stability and mechanical robustness. As shown in Fig. 3, the morphology of the nano-arrays after prolonged high temperature aging does not vary much, with small mass loss observed in the first 24 h. The crystal structures of aged metal oxides nano-arrays retained without phase segregation as revealed by XRD analysis. The measured surface area loss of typical nano-arrays after 100 h  $800\ ^\circ\text{C}$  annealing was much smaller than their counterparts of wash-coated catalysts. For instance, the surface area loss of ZnO nano-arrays was found to be only 5% while that of ZnO wash-coated powders was over 50%.  $\text{TiO}_2$  nano-arrays suffered 40% surface area loss but the  $\text{TiO}_2$  powders lost over 80% of the surface area. The nano-arrays also demonstrate good mechanical integrity under fast air flux ( $50\ \text{L/min}$ ) for 10 days, featuring little morphology destruction and negligible weight loss. All these intriguing properties as well as the high catalytic activity highlighted in Sections 4

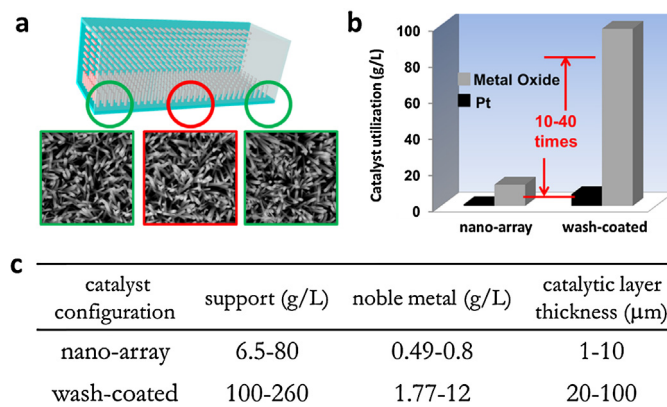


Fig. 2. (a) Schematic and micrographic illustration of the nanostructure arrays in situ grown on the individual channel surface of the monolithic substrate; (b) histogram comparison and (c) summary table of catalyst utilization efficiencies for nano-array based monolithic catalysts and washcoated ones.

Reprinted with permission from Ref. [22].

Download English Version:

<https://daneshyari.com/en/article/53619>

Download Persian Version:

<https://daneshyari.com/article/53619>

[Daneshyari.com](https://daneshyari.com)