RAPID COMMUNICATION

Robust 3-D configured metal oxide nano-array based monolithic catalysts with ultrahigh materials usage efficiency and catalytic performance tunability

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Abstract
Constructed with parallel or honeycomb channels micrometer to millimeter in diameter, monolithic catalysts and reactors have been utilized in various business sectors ranging from mechanical, automotive, fine chemicals, pharmaceutical, to biotechnology industries. However, the performance of state-of-the-art washcoating monolithic catalysts in industry suffers from some long-standing problems such as mediocre-uniformity, need for high catalyst loading, low materials utilization, random catalytic sites, poor washcoat adhesion, short life-time, degradation tendency, all of which lead to much compromised and less-than desirable catalytic performance. In this work, we significantly mitigated these issues and reduced precious metal and metal oxide usages by 10-40 folds, by directly integrating bare monolith structures with ultra-efficient, thermally stable, and physically and chemically well-defined nanostructure arrays. The well-defined nanostructure array monolithic catalysts represent a new and effective model platform for bridging catalytic nanomaterials science and engineering with the practical industrial catalysis.

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Introduction

Heterogeneous catalytic processes are among the major solutions for enhancing materials utilization efficiency, decreasing raw materials consumption and therefore materials cost in chemical industries, fuel cell, fuel production and for efficiently eliminating or reducing pollutant emissions [1]. Discovery and design of cost-effective, efficient, and multifunctional heterogeneous catalysts stands as one of the major challenges facing today's scientists and engineers [2]. As one of the more important catalyst configurations, monolithic catalytic devices, such as catalysts, filters, and reactors, are generally more efficient and cost-effective compared with powder or pellet ones, as a result of a few outstanding merits including low pressure drop, high geometric surface area, efficient mass-transfer, and relatively low catalyst usage [1-3]. Consequently, they have been important devices as either dedicated or alternative solutions in catalytic combustion, chemical production, separation and purification, and environmental pollutant treatment such as water purification, vehicle and industrial exhaust emissions treatment [1c,4]. However, three main issues remain challenging for the research and development of monolithic catalytic devices: (i) the inadequate use of precious metals (Pt, Rh, and Pd) in some applications such as exhaust treatment makes them expensive and limited supply; (ii) Empirical washcoated powder-form catalysts lack the well-defined structural and geometrical configurations, which severely 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, i.e., atomic and nanoscopic surfaces and interfaces in the comprised individual micro- and nanostructures, is quite limited [5]. On the other hand, although various nanostructure (such as nanoparticles, nanowires) based powder-form catalysts have shown promising potential as efficient catalysts [5,6], nanostructure based monolithic catalysts have been rarely investigated due to the lack of effective integration strategy.

Herein, through a general nanostructure array (nano-array) integration approach (Figure. 1a), we have addressed and significantly mitigated the above mentioned issues. Given its great importance in both practical application (e.g., exhaust pollutant treatment, fuel cell) and fundamental research [7], CO oxidation reaction was performed as a probe reaction over the 3-D configured nano-array based monolithic catalysts. Specifically, by using a low-cost, green and robust hydrothermal process, crystalline nano-arrays of support metal oxides such as ZnO, TiO2, CeO2, and Co3O4 have been directly grown onto commercial honeycomb monolithic substrates, which have greatly enhanced the devices' surface area, the array-surface Pt-nanoparticle dispersion and active site population, and demonstrated strong nanostructure-substrate adhesion and tunable nanostructure shape and size. In the meantime, efficient gas diffusion and catalytic reaction have been enabled in these nano-arrays due to the ordered macroporous channels of the array structures. As a result, with 10-40 times less mass loading in both Pt and support metal oxides than classical washcoated powder-form ones, these monolithic catalysts demonstrated consistently excellent, robust, and tunable catalytic CO oxidation performance.

Experimental

Growth of nano-array based monolithic catalysts

A low temperature hydrothermal method was used for the growth of various metal oxide (ZnO, TiO2, Co3O4) nanorod arrays directly onto monolithic substrates. CeO2 nanotube arrays are grown on monoliths using ZnO nanorod arrays as template with additional hydrothermal deposition of CeO2 nanoshells, followed by ZnO template removal by wet chemical etching. The Pt nanoparticles were loaded onto nano-array rooted monoliths using dipping deposition of colloidal Pt nanoparticles made from thermal decomposition of Pt-contained hydrochloride salts. Typically, the required amount of as-prepared Pt colloid (Pt/cordierite=0.1 wt%) was diluted by acetone to the volume which can totally cover the nano-array rooted monoliths. The grown substrates were immersed in the dilute Pt colloid solution for 24 h. Finally, the catalyst samples were dried at 80 °C in air ready for use.

Catalyst evaluation

A BenchCAT reactor (Altamira Instruments) was used for CO oxidation tests. Dycor Dymaxion mass spectrometer and Agilent Micro GC were used for the gas species analysis in the product stream. Oxidation study was carried out in a temperature range of 20-500 °C using 5 sccm of 10% CO/N2, 5 sccm of O2, and 40 sccm of Argon, i.e., 1% CO, 10% O2, 9% N2, and 80% Ar.

Results and discussion

Figure. 1b shows the photographic image of four types of nano-array based monolithic catalysts including ZnO, TiO2, CeO2, and Co3O4. Scanning electron microscope (SEM) top-view images of ZnO nanowire array rooted cordierite monolith channels are shown in Figure. 1c at low magnification. The as-synthesized Co3O4 nanowires (∼10 μm long) in Figure. 1d-e exhibited a high uniformity as well as well-aligned and densely packed array characteristics. The closer view electron micrographs in Figure. 1f-m revealed the well-defined structural and morphological characteristics of the grown metal oxide nano-arrays on monolith substrates. For instance, Figure. 1f (SEM) and 1j (TEM) identified the ZnO nanowire arrays with good uniformity and coverage, single crystallinity, a diameter of ∼60 nm, and [0 0 0 1] growth direction. Table 1 summarizes the physical, chemical, and structural characteristics of the as-grown metal oxide nano-arrays. (see Supporting information “Morphology and Structure of Nanostructure Arrays; Pages S5-S9”).

Thermal and mechanical stability of monolithic catalysts is crucial to various catalytic processes at elevated temperature, such as catalytic combustion, steam reforming, and automobile exhaust aftertreatment [8]. In vehicular applications, the monoliths are also subjected to excessive
mechanical vibrations. Therefore we conduct a series of time dependent studies on thermo-gravimetry, surface area changes, structure and morphology evolution, and mechano-gravimetry. It is noted that the thermal and mechanical stability of two-step template-induced CeO₂ nanotube array (Supporting information "CeO₂ nanotube array monolithic catalysts: thermal and mechanical stability") was not as good as those of the directly grown nanowire array (ZnO, TiO₂, and Co₃O₄) based monolithic catalysts (as illustrated in Figure 2), which is due to the polycrystalline nature of the nanotubes and their non-uniform tube wall thickness along the nanotube length. For the nano-array monoliths based on ZnO, TiO₂, and Co₃O₄, less than 1% mass change was observed after a 100-h 800 °C isothermal annealing process. The corresponding XRD spectra revealed no phase segregation for ZnO, TiO₂, and Co₃O₄ nano-array monoliths. From inset SEM images, the ZnO and TiO₂ nano-array structures remained intact despite the gradually smoothened edges of the nanorods. In Co₃O₄, the as-prepared porous nanowires with relatively smooth surfaces turned into zigzag periodic and rough nanowires after 24 h annealing at 800 °C (Fig. 2c). However, the morphology of Co₃O₄ nanowires retained further after 24 h. The pore size distribution changed little with an average 20 nm pore size maintained throughout the 800 °C isothermal process (Figure. S9), but the pore volume dropped by ~46% after the first 24 h, indicating the decrease of pore population.

The measured BET surface area of TiO₂ nanorod array monolith decreased by ~43%, from 57 m²/g to 33 m²/g after 24-h annealing at 800 °C. After that, surface area stayed constant throughout the remaining 76-h isothermal process.
Similar to TiO$_2$ nanorods, the surface area of Co$_3$O$_4$ nano-wire array monolith decreased from 8 m$^2$/g to 4 m$^2$/g after 24-h annealing at 800 °C. However, the surface area of ZnO nanorod array monolith remained constant in the 100-h annealing at 800 °C. Compared with the significant surface area decrease in conventional powder-form catalysts (50% decrease in ZnO; >80% decrease in TiO$_2$ and Co$_3$O$_4$) under high temperature [9], ZnO, TiO$_2$ and Co$_3$O$_4$ nano-array monoliths demonstrated much higher thermal stability in both short-term and long-term scales (5%, 43%, and 56% surface area decrease for ZnO, TiO$_2$, and Co$_3$O$_4$, respectively). As-prepared nano-array structures also exhibit good thermal stability in reductive atmosphere (see Supporting information “Thermal and mechanical stability; Pages S10-S18”: Fig. S10).

### Table 1

Physical, chemical, and structure characteristics of grown nano-arrays on bare monolith substrates.

<table>
<thead>
<tr>
<th>Material</th>
<th>Array morphology</th>
<th>Diameter (nm)/length (µm)</th>
<th>Wall thickness or pore size (nm)</th>
<th>Structure/crystallinity</th>
<th>Growth direction</th>
<th>d-spacing (nm)/crystal plane</th>
<th>Images (Fig. 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>Nanorod/nanowire</td>
<td>50-150/1-5</td>
<td>1-5</td>
<td>Wurtzite/single crystal</td>
<td>[0 0 0 1]</td>
<td>0.52/[0 0 0 1]</td>
<td>c, f, j</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Nanorod</td>
<td>50-130/0.5-1</td>
<td>-</td>
<td>Brookite/single crystal</td>
<td>[0 0 1]</td>
<td>0.35/[1 1 0]</td>
<td>g, k</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>Nanotube</td>
<td>70-200/1-5</td>
<td>10-20</td>
<td>Fluorite/polycrystal</td>
<td>-</td>
<td>0.31/[1 1 1]</td>
<td>h, l</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>Porous nanowire</td>
<td>100-200/1-12</td>
<td>20 (10-50)</td>
<td>Spinel/polycrystal</td>
<td>-</td>
<td>0.46/[1 1 1]</td>
<td>d, e, i, m</td>
</tr>
</tbody>
</table>

Figure 2  Thermal and mechanical robustness of metal oxide nano-array based monolithic catalysts in ambient atmosphere. Time dependent Thermo-Gravimetric Analysis (TGA), Brunauer-Emmett-Teller (BET) specific surface area, morphology and crystal phase change, and time dependent morphology and weight loss at constant air flow of 50 L/min. Plots: (a) 1 µm ZnO nanorod array grown on stainless steel monolith. (b) 1 µm TiO$_2$ nanorod array grown on cordierite monolith. (c) 8 µm Co$_3$O$_4$ porous nanowire array grown on cordierite monolith. Scale bar: 100 nm for SEM insets in all thermal and mechanical tests in (b); 1 µm for SEM insets in the mechanical tests in (a) and (c).
The well-separated but densely-packed nano-arrays effectively defined and utilized spaces between individual nanostructures with high surface area, therefore suppressing the sintering induced densification and grain growth.

The nano-array adhesion and structure stability was examined by applied high velocity air flow (static 50 L/min or pulsatile flow) for 10 days with monitored morphological variation and weight loss. The results summarized in the right panel of Figure 2 suggested that ZnO, TiO2, and Co3O4 nano-array monoliths exhibited excellent mechanical robustness and the nano-array morphology retained with little change throughout. The weight losses of above three nano-array monolithic catalysts were less than 1% individually.

The rational design and assembly of metal-metal oxide interface through shape and size control is emerging as one of the most effective routes to tailor the catalysts’ surface atomic and electronic structures and thus their catalytic activity and selectivity [5]. Fig. 3a-d displayed the individual ZnO, TiO2, CeO2, and Co3O4 nanostructures loaded with well-dispersed 2 nm Pt nanoparticles on their well-defined crystal surfaces with the inset lattice images clearly identifying the exposed Pt(1 1 1) atomic planes. The light-off temperatures (where 50% of CO conversion is achieved) for CO oxidation of Pt-loaded CeO2, ZnO, Co3O4, and TiO2 nano-array monolithic catalysts are 193 °C, 260 °C, 195 °C, and 258 °C, respectively, and the 100% CO conversion was achieved below 300 °C (Figure 3e). The better CO oxidation performance in Pt/CeO2 nanotube and Pt/Co3O4 porous nanowire array is due to the promotion effect of Co3O4 and CeO2 nanostructure support to Pt nanoparticle [10]. Figure 3f shows the ZnO, Co3O4, and TiO2 nano-array supported Pt monolithic catalysts all displayed a very stable 100% CO conversion to CO2 at T100 throughout the 24 h. In Pt/CeO2 nano-array catalysts, 100% CO conversion
only sustained the initial 6 h. The catalytic activity degradation is caused by its relatively lower thermal and mechanical stability (Supporting information “CeO2 nanotube array monolithic catalysts: thermal and mechanical stability”). The loaded Pt nanoparticles on the nano-array monolithic catalysts show little change in size with well-retained nano-array structure for both ZnO and TiO2 after the catalytic performance and stability tests (Figure. S14), demonstrating their excellent thermal stability.

Compared with the reported washcoated powder catalysts with comparable performance [11], the materials utilization efficiency of our nano-array monolithic catalysts (Figure. 3g) is ∼10-40 times higher with extremely small loadings of precious metal and metal oxide nano-arrays used (Supporting information “CO oxidation; Pages S18-S29”: Tables S4-S6).

It has been predicted that by introducing of macropore into mesoporous catalysts, 20-40% less usage of catalytic material but 80-180% higher activity than the purely mesoporous catalysts can be achieved [12a]. Moreover, the reactivity of optimally arranged pore architecture can be 8-10 times better than random pores [12b,c]. The 3-D configured nano-arrays have intrinsically ordered macropores between adjacent nanostructures, which form ordered and macroporous channels. These ordered and macroporous channels not only enable optimum metal loading and dispersion during catalyst preparation, but also better expose the active sites and promotes gas-solid
interaction by a much shorter diffusion length (Fig. 3h), as experimentally confirmed in the Pt/ZnO nano-array catalysts (Figure. 4). Besides, the mesoporous nanostructure/Pt nanoparticle interfaces may allow more effective charge transport and thus enhanced reaction efficiency.

The clear purview of morphology and metal-metal oxide support interaction interaction dependence of catalytic activity in nanostructured catalysts holds crucial importance in their rational design, synthesis, and application. To gain such understanding, however, is a non-trivial task. Here we use the Pt/ZnO nano-array catalysts as a model platform to practically investigate the catalytic activity dependence on the nanostructure size, shape (crystal facets), macropore distribution, and metal-support interaction.

Different ZnO nanostructure coated monolithic samples were fabricated as shown in Figure. 4a-d. With similar Pt loading, 5.5 μm ZnO nanorod array monolithic catalysts exhibited better CO oxidation catalytic activity than 1 μm ZnO nanorod array, and both of them were better than washcoated ZnO powder monolithic catalysts with similar materials loading (Figure. 4e). The T_{100} temperature of 5.5 μm Pt/ZnO nanorod array decreased by ~10 °C (220 °C), and light-off (T_{50}) and conversion (T_{100}) temperatures decreased by ~30 °C compared to those of the 1 μm one, which are also ~20 °C lower than those of the washcoated powder catalysts. The calculated catalytic activities (mmol CO_{2} per gram of Pt) at 230 °C (below 100% conversion) are 4.1 and 1.1 for the 5.5 μm and 1 μm Pt/ZnO nanorod arrays, respectively, about 2-7 times more active than the washcoated Pt/ZnO powder catalysts (0.56) (Table S3). This activity difference between nano-array and washcoated powder catalysts confirmed that the ordered macropore distribution might play an important role to improve the catalytic activity. The CO conversion efficiency enhancement with increasing nanowire length may be due to a higher dispersion of Pt nanoparticles on longer ZnO nanowires, associated with their increased chance for strong ZnO-Pt interaction and more exposed active sites [13]. On the other hand, to investigate the shape dependence of catalytic behavior, ZnO nano-arrays made of nanorods and nanoplates with same mass loading were uniformly grown on monolithic substrates. These catalysts have predominant {0 0 0 1} or {0 1 1 0} crystal surfaces, with identical mass loading over ZnO nano-arrays, normalized amount, crystallinity and size of Pt nanoparticles. The CO light-off curves in Fig. 4f clearly suggest that, Pt/ZnO nanoplate array has a ~20 °C lower T_{100} (242 °C) than ZnO nanorod array catalysts. Given the identical experimental parameters control, the catalytic activity difference between the nanoplate and nanorod catalysts is due to the different crystal surface area ratio of {0 0 0 1} to {1 0 0 1} (inset of Fig. 4f), i.e., the different Pt-ZnO facets interaction effect. The interaction of Pt and Zn^{2+} could lead to localized electron transfer on Zn-terminated (0 0 0 1) surface, resulting in lower CO desorption temperature responsible for the lower CO oxidation temperature in Pt/ZnO nanoplate than that of Pt/ZnO nanorod [14].

Conclusions

In summary, the metal oxide nano-array based monolithic catalysts represent a new and effective model platform for bridging catalytic nanomaterials science and engineering with the practical industrial catalysis, and enhancing the predictive catalysis science through the enabled exacting relations between tunable nanomaterials size, shape, structure, tailorable metal-support interaction, and multifunctional catalytic performances. It is worth pointing out that a wide spectrum of single-component or multi-component nano-array building blocks can be integrated with various geometrical, chemical, structure, and functional properties for the nano-array monolithic devices [15] (Supporting information SI “Morphology and Structure of Nanostructure Arrays; Pages S5-S9”). Therefore, the 3-D configured nano-array based monoliths provide a general strategy for integration of different functional nano-structure arrays with commercially available monolithic substrates, and may bring up a broad array of nanostructure based monolithic devices with ultra-efficient, robust, and multi-functional performance for various catalytic energy, environmental, and biotechnology applications.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2013.03.004.

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