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Synthesis and growth behavior of $CeO_2/ZrO_2/LaAlO_3$ nanorods on hierarchical macroporous γ-alumina monoliths

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ABSTRACT

Different kinds of metal oxide nanorods (CeO_2, ZrO_2 and $LaAlO_3$) grown on hierarchical macroporous γ-alumina monolith with excellent thermostability and mechanical strength are successfully synthesized by combining sol-gel method with boiled water-bath crystallization. Different kinds of metal oxide nanorods have different growth behavior. Monolayer stripe CeO_2 nanorods with approximately equal length accumulated by nanoparticles covered mainly on the surface of the skeleton. Minor ZrO_2 nanoparticles not only accumulated on the surface but also grew on hollow and conjunct part of the skeleton as well as the internal surface of the pore channels in a stagger and grid way. While the $LaAlO_3$ crystal particles were grown mainly on the skeleton surface of alumina monolith but hardly any on the internal surface. In addition, the dipping time and temperature of metal ions have important effects on the nanoparticles morphology. The unique combination of excellent support and auxiliaries candidates can be used as promising functional materials in the field of heat/mass transfer, microchannel and separation especially in heterogeneous catalysis.

1. Introduction

Hierarchical porous materials have widely potential applications in catalysis, separation and purification as well as electronic devices because of their unique pore structures, high surface areas and high mechanical strength. Huge progress has been made in the development of synthetic methods [1–4] and pore structure designing [5–7] with different pore dimensions from nano-scale micropores, mesopores to macropores. Increasing references identified the contributions of multilevel porous architectures to the unique properties and potential functions for the as-synthesized materials, e.g. micro- and mesopores impart high surface areas and pore volumes providing size and shape selectivity and high surface areas, while larger pores reduce transport limitations in the material and facilitate mass transport to the active sites [8]. Various preparation techniques such as nanocasting, foaming and sol-gel processing have been reported for the preparation of hierarchical materials, of which sol-gel processing along with phase separation are extremely emphasized. Kinds of monoliths including silica, alumina, titania, tungsten oxide and their composite have been synthesized by phase-separation-induced sol-gel method [9–13]. Alumina monolith was considered to be one of the most promising applicable materials since γ-alumina was recognized as the most common catalyst supports. Results in our previous work demonstrated that unique hierarchical porosity structure of Al_2O_3 monolith-supported catalysts can significantly improve the activity in methane combustion [14]. Commonly, not only characteristics including activity and specific surface area of supports, but also amount and species of auxiliaries play an important role in the performance of supported catalysts. Nice auxiliary candidates can improve thermal stability of supports and the interaction between supports and active component thus enhance the catalytic activity of the catalysts. Cerium, zirconium and lanthanum attracted more fascinating interest as auxiliaries for supported catalysts and exhibited excellent performance in various catalytic reactions such as methane combustion [15,16], reforming of methane to syngas [17], steam reforming of vegetable oil [18] and automobile exhaust gas treatment [19].

In this study, we report a controllable growth path of CeO_2, ZrO_2 and $LaAlO_3$ nanocrystals onto the alumina monolith skeleton and investigate their growth behavior and probable interaction. By incorporating hierarchical well-defined three-dimensional macroporous structures with homogeneous dispersion nanorods in one unit, the new composite materials coupling the excellent support and auxiliary candidates can have promising applications for various catalytic reactions.

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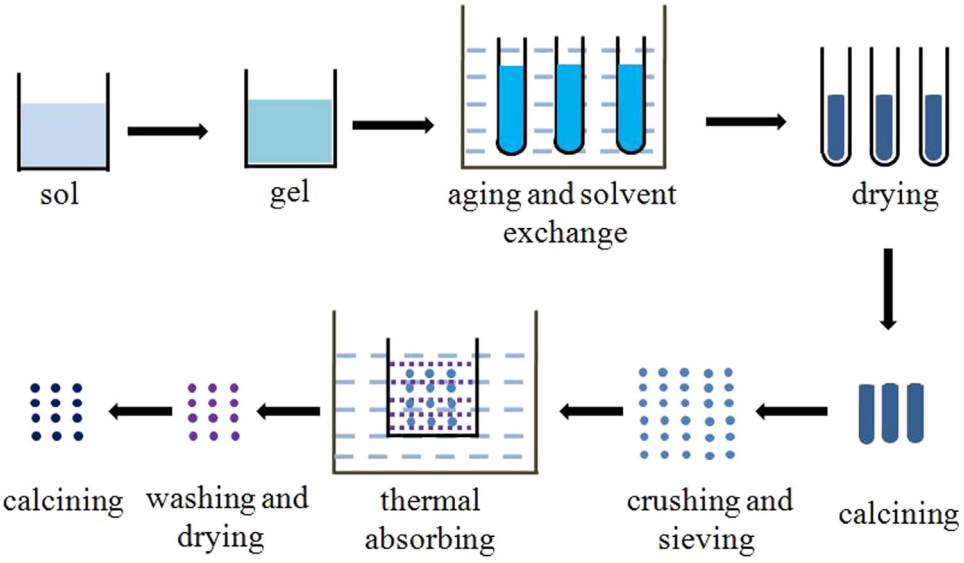

Fig. 1. Schematic illustration of the synthetic process of Al_2O_3 monoliths.

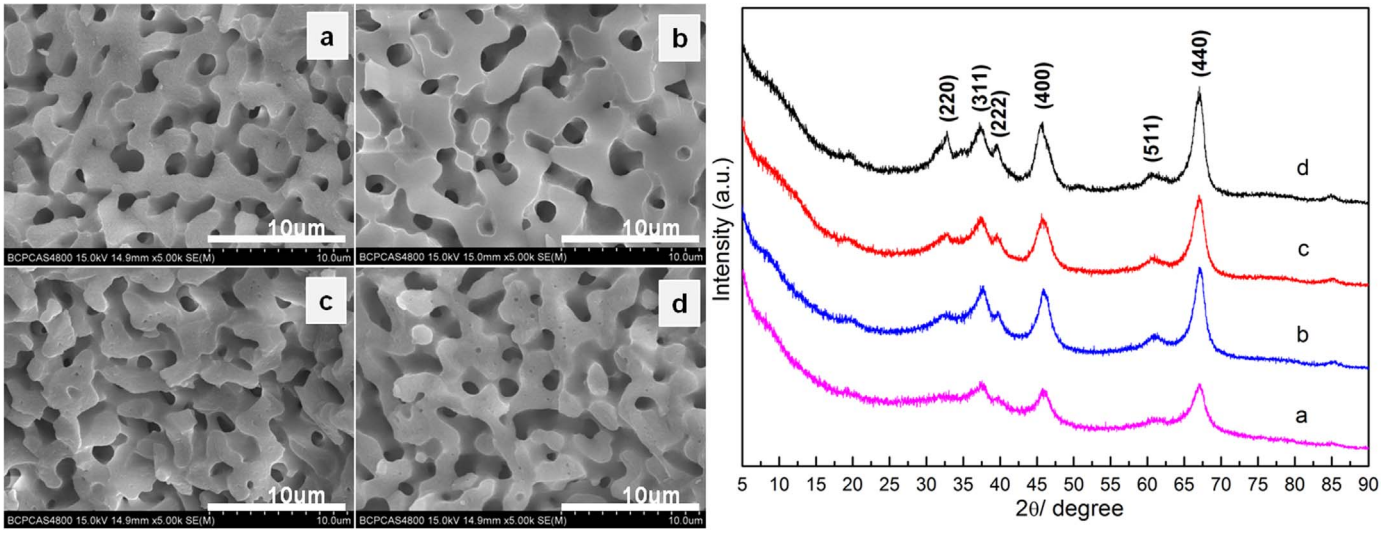

Fig. 2. SEM and XRD patterns of alumina calcined at 973 K (a), 1073 K (b), 1173 K (c), 1273 K(d).

2. Experimental

2.1. Chemicals

Ethanol, HNO_3, $Ce(NO_3)_3{\cdot}6H_2O$, $Zr(NO_3)_4{\cdot}5H_2O$, $La(NO_3)_3{\cdot}6H_2O$, were acquired from Beijing Chemical Co., $AlCl_3$, $Al(NO_3)_3$, propylene oxide(PO) were from Shantou Xilong Chemical Co., Guangdong. All chemicals were of analytical-grade without further purification.

2.2. Synthesis

Alumina monoliths were typically synthesized via sol-gel preparation process during which polyethylene oxide was employed as the phase separation agent [14]. Fig. 1 schematically shows the synthetic process.

After calcination, the monoliths were crushed and sieved to 40–60 mesh and divided into two parts. One was dipped into the 1 M nitric acid solution of $Ce(NO_3)_3{\cdot}6H_2O$, $Zr(NO_3)_4{\cdot}5H_2O$ and $La(NO_3)_3{\cdot}6H_2O$ with pH 3–3.5 and concentration 5% respectively at room temperature for 24 h. Another was dipped into boiled solution by water-bath for 20 min, 40 min and 1 h to improve the dipping effect of the solution into the original monoliths pore channels. Both the two parts were dried and calcined at 823 K for 2.5 h after dipping treatment.

2.3. Characterization

A scanning electron microscope (SEM: HITACHI S-4800, Japan) was employed to examine the morphology of the samples. The X-ray diffraction (XRD) patterns were obtained with Bruker D8-Advance