Fabrication of spinel nanostructured $Mn_xCo_{3-x}O_4$ sheet array based monolithic catalysts for low temperature propylene and propane oxidation

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Introduction

In the past few decades, the state-of-art washcoat technology has been successfully used for fabricating catalytic convertors in automotive emission control industry. However, there are still some challenges for application of powder-based nanomaterials in washcoat process: a) the relatively dense coated layer cannot fully meet the requirement of mass transfer under harsh condition like high space velocity; b) catalytic performance and materials utilization efficiency will be compromised by the lack of well-defined structure; c) nanostructure-derived properties can be kept very well during the coating procedure. Recently, a series of metal oxide (ZnO, Co_3O_4, $NixCo_{3-x}O_4$, CeO_2 and MnO_2 etc.) nanostructure array (nano-array) based monolithic catalysts have been developed in our group[1-3]. The integration of 3-D catalytic metal oxide nano-arrays onto 3-D channel surfaces of monolithic honeycomb can significantly reduce the catalyst usage by taking full advantages of the nanostructure-derived properties without sacrificing the catalytic activities. The nano-arrays with high surface area provide a highly active interface and a special space constructed by array units offer a versatile environment for efficient mass transfer and catalytic reactions. Herein, a new reaction between $KMnO_4$ and $Co(NO_3)_2$ was developed to *in situ* grow spinel $Mn_xCo_{3-x}O_4$ sheet nano-array on 3-D channeled cordierite honeycomb at a large scale. By modifying the surface of cordierite substrate, the geometrical configuration can be readily adjusted toward low-temperature catalytic oxidation of hydrocarbons.

Materials and Methods

The nanostructured $Mn_xCo_{3-x}O_4$ sheet array was synthesized by a hydrothermal reaction between $KMnO_4$ and $Co(NO_3)_2$ solution. Two kinds of cordierite honeycomb (600 cpsi) including blank one and another treated with basic solution were used as the substrates to in-situ grow nano-array based catalysts. The catalytic hydrocarbons combustion was conducted in a fixed-bed reactor by using the BenchCAT system with a space velocity of 24,000 h^{-1}. The typical reaction gas was 0.5% C_3H_6 (or 0.3% C_3H_8) +10% O_2 balanced with nitrogen.

Results and Discussion

Compared to the blank cordierite honeycomb (Fig. 1a), a uniform nano-sheet array (Fig. 1c) was etched out after the basic solution treatment, which made the surface rougher. By using the blank and etched cordierite as a growing substrate, highly uniform $Mn_xCo_{3-x}O_4$ nano-array films (MnCo-1) assembled by numerous nano-sheets could be successfully introduced on the substrate surface with good adhesion property. Obviously, the nano-sheets grown on the etched cordierite (MnCo-2) shows bigger size and low density, and the thickness (3 μm) is much higher than that (500 nm) on the blank cordierite as shown in the inset images. The BET analysis in Figs. 1 e and f reveals more porous structure displayed (high surface area and wide pore distribution) on the MnCo-2 that may lead to a better catalytic performance due to the higher concentration of active sites and better mass transfer environment. As displayed in Figs. 1 g and h, the complete propylene and propane conversion over MnCo-2 can be observed at temperature as low as 275 and 350 °C, which is 50 and 125 °C lower than that of MnCo-1. More analysis has been carried out to investigate the relationship among textural properties, mass transfer, surface chemistry and reaction activities.

Significance

A new reaction between $KMnO_4$ and $Co(NO)_2$ has been firstly found to synthesize Mn-Co spinel oxide and it is successfully applied to in-situ grow $Mn_xCo_{3-x}O_4$ sheet array film on the 3-D channel of commercial cordierite honeycomb. The textural properties can be controlled by modifying the surface of cordierite substrate. By adjusting the porosity of $Mn_xCo_{3-x}O_4$ sheet array, the catalytic activities toward hydrocarbons combustion can be significantly promoted.

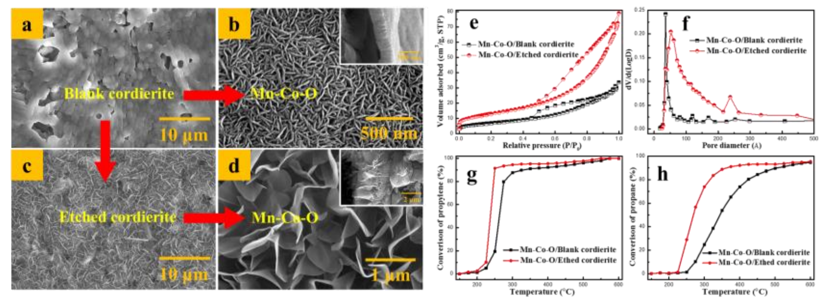

Figure 1. (a and c) Blank cordierite and etched cordierite surface; (b and d) Top view and cross section (inset image) of Mn-Co-O nanoarray on blank cordierite and etched cordierite; (e and f) N_2 adsorption-desorption isotherms and pore-size distribution of Mn-Co-O nanoarray based monolith; (g-h) catalytic propylene and propane oxidation performance of Mn-Co-O nanoarray based monolith.

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