Morphologically uniform Co$_3$O$_4$ hexagonal plates of the (112) facets with surface Fe/Mn doping and Au loading: Exceptionally active for catalytic combustion of benzene

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1. Introduction

Recent studies demonstrated that morphology or facet structure control is a powerful approach to achieving highly active, selective, yet durable catalyst systems for various applications. Catalytic removal of VOCs is a very important topic for environmental protection. Developing highly efficient Co-based catalyst becomes a hot spot for this kind of reaction. In the present study, we first synthesized the hexagonal plates of β-Co(OH)$_2$ precursor and further obtained the morphologically uniform Co$_3$O$_4$ hexagonal plates of the (112) facets which is already very active for the target reaction. Simple doping of the structurally defined Co$_3$O$_4$ substrate with Fe or Mn element can yield the morphology-retained Mn$_x$Co$_{3-x}$O$_4$ and Fe$_x$Co$_{3-x}$O$_4$ hexagonal plates with enhanced catalyst performance. With following precise Au deposition (~3 nm) of narrow particle size distribution, extremely active Au/Mn$_x$Co$_{3-x}$O$_4$ and Au/Fe$_x$Co$_{3-x}$O$_4$ are achievable with the lowest T$_{100}$ of 195 °C known to date for benzene combustion.

2. Experimental

(1) Synthesis of β-Co(OH)$_2$ precursor: CoCl$_2$·6H$_2$O of 7.12 g was dissolved in 100 ml distilled water under a N$_2$ flow (100 ml min$^{-1}$). After that, NaOH of 4 g was dissolved in 40 ml water and the solution was added drop wise into the first solution under stirring. The mixture was divided into two parts and subjected to a hydrothermal treatment at 180 °C for 24 h. The precipitate was collected and washed with distilled water.

(2) Synthesis of Co$_3$O$_4$ hexagonal plates: Air calcination of β-Co(OH)$_2$ precursor was performed at 400 °C.

(3) Synthesis of Mn$_x$Co$_{3-x}$O$_4$ and Fe$_x$Co$_{3-x}$O$_4$ hexagonal plates: In preparation of β-Co(OH)$_2$ precursor, part of CoCl$_2$ was replaced by MnCl$_2$ or FeCl$_3$, with the molar ratio of Mn (or Fe) : Co = 3:97, 6:94, 9:91 and 12:88. The samples M$_x$Co$_{97-x}$O$_4$, M$_x$Co$_{94-x}$O$_4$, M$_x$Co$_{90-x}$O$_4$ and M$_x$Co$_{86-x}$O$_4$ (M = Mn or Fe) were received. (4) Preparation of Au-loaded samples: Deposition-precipitation method was employed to load Au species on Co$_3$O$_4$ plates and doped substrates with a nominal Au loading being 3% by weight. The product was collected by centrifugation, dried at RT overnight, and calcined at 250 °C for 2 h. The samples were characterized by XRD, SEM, TEM, H$_2$-TPR and evaluated for benzene combustion.

3. Results and discussion

A series of Co$_3$O$_4$, Mn$_x$Co$_{3-x}$O$_4$, and Fe$_x$Co$_{3-x}$O$_4$, together with the Au-deposited interfacial structures were achieved via the controllable synthesis approaches. The primarily exposed facet was identified to be (112) over pure Co$_3$O$_4$ hexagonal plates, which exhibited excellent catalytic activity for benzene combustion (T$_{100}$ = 240 °C). When the pure Co$_3$O$_4$ hexagonal plates were doped with Mn or Fe element, even with a low content, the resulting M$_x$Co$_{97-x}$O$_4$, M$_x$Co$_{94-x}$O$_4$, M$_x$Co$_{90-x}$O$_4$, and M$_x$Co$_{86-x}$O$_4$ (M = Mn or Fe) would not only maintain the original sample morphology but also improve catalyst performance. Among them, Mn$_x$Co$_{94-x}$O$_4$ and Fe$_x$Co$_{90-x}$O$_4$ were found to be the most effective for the reaction. T$_{100}$ was notably reduced to 215 °C and 225 °C respectively for Mn$_x$Co$_{94-x}$O$_4$ and Fe$_x$Co$_{90-x}$O$_4$. With precise Au loading over Fe$_x$Co$_{90-x}$O$_4$, the catalytic activity of benzene combustion was further considerably enhanced, with the T$_{100}$ be reduced to 195 °C over Au/Fe$_x$Co$_{90-x}$O$_4$. TEM images shown in Fig. 1 demonstrated that although the Mn or Fe doping does not cause morphology variation of sample but significantly decreased the plate dimension, resulting in a remarkable increment in surface area of substrate. (HR)TEM image of the Au-loaded sample indicated that Au
deposition had little impact on the facet structure of substrate. The doping element, however, showed direct influence on the interfacial catalysis of Au/MnCoOx system.

Scheme 1. The preparation of Co3O4 hexagonal plates and benzene combustion over Au/Co3O4.

Figure 1. (A1-A3) SEM, TEM, HRTEM of Co3O4 hexagonal plates, respectively. (A4-A5) HRTEM of Au/Co3O4. (B) ball-stick model (left) and polyhedral model (right) of cell structure of spinel, (C1-C4) SEM images of Mn3Co97Ox, Mn6Co94Ox, Mn9Co93Ox, and Mn12Co88Ox respectively, (D1-D4) SEM images of Fe3Co97Ox, Fe6Co94Ox, Fe9Co93Ox, and Fe12Co88Ox respectively.

Figure 2. The effect of Mn (Fe) doping and Au loading on catalyst performance.

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References