Morphologically uniform Co_3O_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_3O_4 hexagonal plates of the (112) facets which is already very active for the target reaction. Simple doping of the structurally defined Co_3O_4 substrate with Fe or Mn element can yield the morphology-retained $Mn_xCo_{3-x}O_4$ and $Fe_yCo_{3-y}O_4$ hexagonal plates with enhanced catalyst performance. With following precise Au deposition (~ 3 nm) of narrow particle size distribution, extremely active Au/$Mn_xCo_{3-x}O_4$ and Au/$Fe_yCo_{3-y}O_4$ 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: $CoCl_2 \cdot 6H_2O$ 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 ℃ for 24 h. The precipitate was collected and washed with distilled water. **(2) Synthesis of Co_3O_4 hexagonal plates:** Air calcination of β-$Co(OH)_2$ precursor was performed at 400 ℃. **(3) Synthesis of $Mn_xCo_{3-x}O_4$ and $Fe_yCo_{3-y}O_4$ hexagonal plates:** In preparation of β-$Co(OH)_2$ precursor, part of $CoCl_2$ was replaced by $MnCl_2$ or $FeCl_2$, with the molar ratio of Mn (or Fe) : Co = 3:97, 6:94, 9:91 and 12:88. The samples $M_3Co_{97}O_x$, $M_6Co_{94}O_x$, $M_9Co_{93}O_x$, and $M_{12}Co_{88}O_x$ (M = Mn or Fe) were received. **(4) Preparation of Au-loaded samples:** Deposition-precipitation method was employed to load Au species on Co_3O_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 ℃ 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_3O_4, $Mn_xCo_{3-x}O_4$, and $Fe_yCo_{3-y}O_4$, 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_3O_4 hexagonal plates, which exhibited excellent catalytic activity for benzene combustion (T_{100} = 240 °C). When the pure Co_3O_4 hexagonal plates were doped with Mn or Fe element, even with a low content, the resulting $M_3Co_{97}O_x$, $M_6Co_{94}O_x$, $M_9Co_{93}O_x$, and $M_{12}Co_{88}O_x$ (M = Mn or Fe) would not only maintain the original sample morphology but also improve catalyst performance. Among them, $Mn_6Co_{94}O_x$ and $Fe_6Co_{94}O_x$ were found to be the most effective for the reaction. T_{100} was notably reduced to 215 °C and 225 °C respectively for $Mn_6Co_{94}O_x$ and $Fe_6Co_{94}O_x$. With precise Au loading over $Fe_6Co_{94}O_x$, the catalytic activity of benzene combustion was further considerably enhanced, with the T_{100} be reduced to 195 ºC over Au/$Fe_6Co_{94}O_x$. 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/$M_6Co_{94}O_x$ system.

Scheme 1. The preparation of Co_3O_4 hexagonal plates and benzene combustion over Au/Co_3O_4.

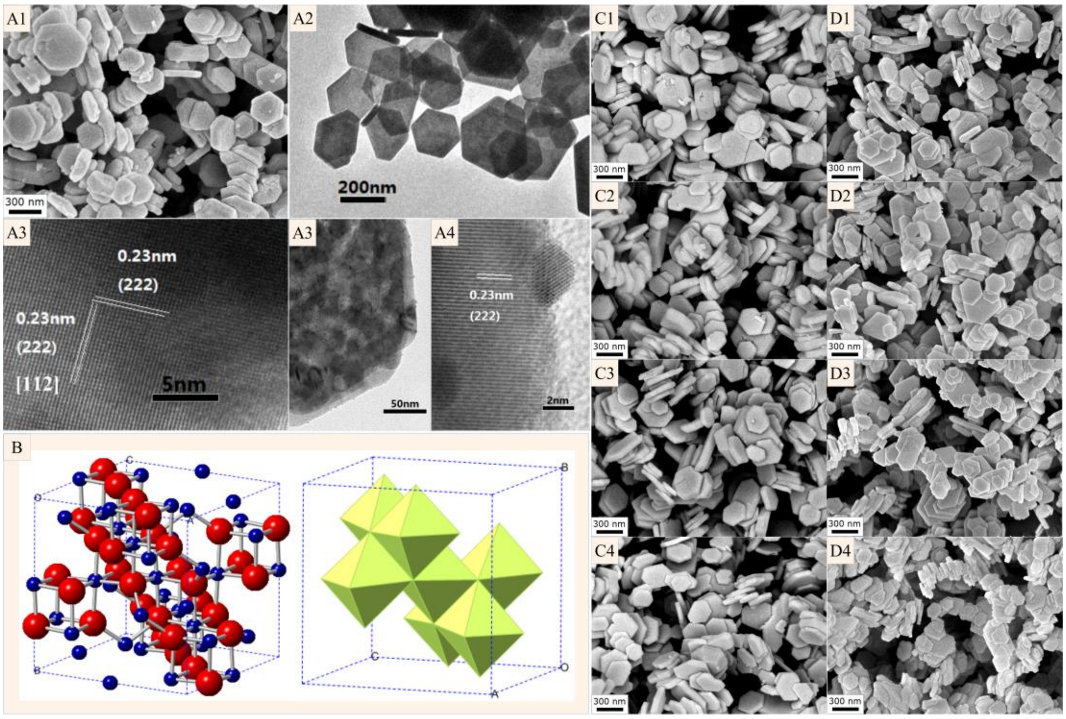

Figure. 1. (A1-A3) SEM, TEM, HRTEM of Co_3O_4 hexagonal plates, respectively. (A4-A5) HRTEM of Au/Co_3O_4, (B) ball-stick model (left) and polyhedral model (right) of cell structure of spinel, (C1-C4) SEM images of $Mn_3Co_{97}O_x$, $Mn_6Co_{94}O_x$, $Mn_9Co_{93}O_x$, and $Mn_{12}Co_{88}O_x$ respectively, (D1-D4) SEM images of $Fe_3Co_{97}O_x$, $Fe_6Co_{94}O_x$, $Fe_9Co_{93}O_x$, and $Fe_{12}Co_{88}O_x$ respectively.

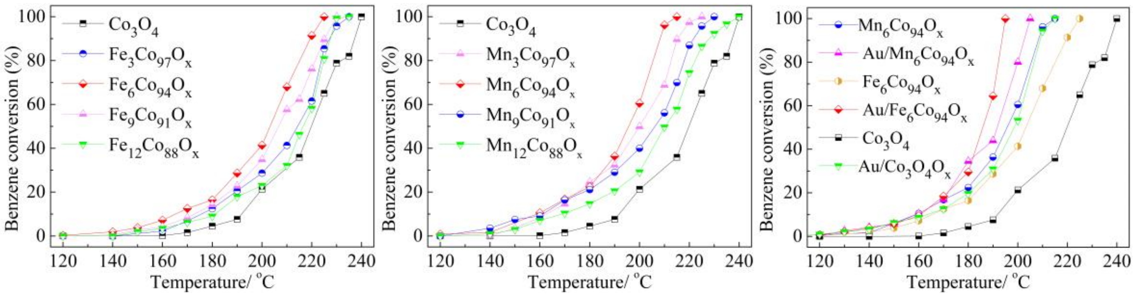

Figure 2. The effect of Mn (Fe) doping and Au loading on catalyst performance.

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