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Short communication

$NiCo_2O_4$ nanoneedle-assembled hierarchical microflowers for highly selective oxidation of styrene

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ABSTRACT

$NiCo_2O_4$ nanoneedle-assembled microflowers have been prepared by a facile one-pot hydrothermal route. The $NiCo_2O_4$ microflowers have a well-defined three-dimensional (3D) hierarchical mesoporous structure. When used as catalysts for the styrene oxidation, the 3D $NiCo_2O_4$ microflowers show a markedly high styrene conversion of 99% and a high selectivity of 80% to styrene oxide (SO). In addition, the $NiCo_2O_4$ catalysts exhibit good recycling stability. The excellent catalytic performance of the $NiCo_2O_4$ catalysts can be owing to the numerous surface active sites caused by the 3D hierarchical mesoporous structure and the possible synergistic effect between nickel and cobalt ions.

1. Introduction

Transitional metal oxides such as Co_3O_4, CoO, NiO and Fe_3O_4 have been the research focus for decades because of their wide applications in many fields (catalysis, sensors, energy conversion and storage, et al.) [1–6]. The magnetic properties of these materials (e.g., Co_3O_4 and $NiCo_2O_4$) make them intriguing catalysts for liquid phase reactions, as these materials can be easily extracted from the reaction solutions by magnetic separation [7,8]. Among them, cobalt-nickel oxide ($NiCo_2O_4$), as an interesting mixed-valence transition metal oxide with a spinel structure, has attracted much attention [9,10]. Importantly, compared with single metal oxides (e.g., NiO and Co_3O_4), the binary metal oxide $NiCo_2O_4$ usually displays higher electrical conductivity and higher catalytic activity [11–14]. On the other hand, the performance of a material in many applications is highly dependent on its morphology and architecture [3,15,16]. A variety of $NiCo_2O_4$ materials with advanced structures have been explored, such as one-dimensional (1D) structures (e.g., nanowires [17] and nanorods [18]), two-dimensional (2D) structures (e.g., nanoflakes [19] and nanosheets [13]) and three-dimensional (3D) structures (e.g., urchin-like structure [20] and foam-like structure [21]). In particular, 3D structures, often assembled from 1D and/or 2D structures, have more advantages such as large specific surface area, abundant interconnected pores for efficient mass transport/diffusion, and rich accessible active sites [13,22].

The catalytic oxidation of alkenes has been an unceasing topic in the chemical industry, and the products epoxides are important raw materials for the chemical industry [23–25]. The catalytic oxidation of styrene to SO has been proposed by the research community because the traditional production method of SO uses peracids that are expensive, corrosive, hazardous and non-selective to SO [26,27]. So far, various catalysts, including homogeneous and heterogeneous catalysts, have been explored for the selective oxidation of styrene to SO. Compared with homogeneous catalysts [28], heterogeneous catalysts can greatly simplify the manufacturing process [29]. Heterogeneous metal oxide catalysts such as CeO_2 [30], Mn_3O_4 [31], NiO [32], Co_3O_4 [31], $SrFe_2O_4$ [7], and $Mg_{0.5}Cu_{0.5}Fe_2O_4$ [33] have been of high interest owing to their low cost and earth abundance. However, these metal oxide catalysts exhibit low styrene conversion and poor selectivity to SO. It is thus of high importance to develop novel metal oxide catalysts with high styrene conversion and selectivity to SO.

In this study, we report on the facile synthesis of the 3D hierarchical $NiCo_2O_4$ microflowers assembled from the $NiCo_2O_4$ nanoneedles. To the best of our knowledge, this is the first report that $NiCo_2O_4$ is used as a catalyst for styrene oxidation reaction (SOR). The catalytic properties of the $NiCo_2O_4$ microflowers over SOR have been comprehensively investigated and discussed. The $NiCo_2O_4$ microflowers exhibit a high styrene conversion and a high selectivity to SO.

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2. Experimental

2.1. Preparation of the $NiCo_2O_4$ and Co_3O_4 catalyst

All the chemical reagents are of analytic grade and used without further purification. Deionized (DI) water was used throughout the experiments.

The $NiCo_2O_4$ hierarchical microflowers were prepared via a facile one-pot hydrothermal method, followed by a pyrolysis process. Typically, 0.73 g of $Ni(NO_3)_2{\cdot}6H_2O$ and 1.45 g of $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in 60 mL of DI water. Under vigorous stirring, 0.8 g of polyvinylpyrrolidone (PVP, K30) was added to the above solution, followed by stirring for 1 h. Then 1.20 g of $CO(NH_2)_2$ was added into the solution. Finally, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave for hydrothermal reaction at 180 °C for 8 h. After cooling down to room temperature, the sample was collected by filtration, washed with DI water and ethanol several times, dried at 80 °C for 5 h, and finally calcined at 500 °C for 2 h. For comparison, the Co_3O_4 was synthesized under similar conditions with $Ni(NO_3)_2{\cdot}6H_2O$ absent in the reaction solution.

2.2. Catalyst characterization

X-ray diffraction (XRD) analysis was conducted on a D8 Advance diffractometer, using Cu Kα radiation (λ = 0.154178 nm). The chemical compositions of the samples were analyzed by X-ray fluorescence (XRF) on a ARL Quant'X XRF analyzer. The morphologies of the samples were characterized by a field-emission scanning electron microscopy (SEM, Hitachi S-4800). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained on a JEM-2100 microscope, equipped with an energy-diffusive X-ray spectroscopy (EDS) attachment. The N_2 adsorption and desorption isotherms were collected at 77 K on a Quantachrome Autosorb-iQ3.

2.3. Catalyst test

The catalysts were employed for the selective oxidation of styrene in a 100 mL round bottom flask equipped with a reflux condenser. In a typical SOR, 15 mmol of styrene and a certain amount of *tert*-butyl hydroperoxide (TBHP) were added to a mixture of 100 mg of catalyst and 16 mL of acetonitrile in the flask under vigorous stirring. After that, the flask was immersed in a water bath at a fixed temperature. The reaction mixture was sampled once an hour. After centrifugation, the products of the reaction were analyzed by a gas chromatography (GC) with a KB-1 column.

3. Results and discussion

3.1. Morphology and structure characterization

Fig. 1 presents the XRD patterns of the $NiCo_2O_4$ and Co_3O_4. Both $NiCo_2O_4$ and Co_3O_4 were crystallized after calcination at 500 °C as evidenced by the diffraction peaks. The $NiCo_2O_4$ and Co_3O_4 display similar XRD patterns, and no diffraction peaks of NiO were detected. This indicates the successful incorporation of Ni ions into the Co_3O_4. The representative peaks at 2θ of 18.9, 31.1, 36.7, 44.6, 59.1 and 65.0° can be indexed as (111), (220), (311), (400), (511) and (440) planes of the spinel $NiCo_2O_4$ (JCPDS 20-0781) and the spinel Co_3O_4 (JCPDS 42-1467), respectively. In addition, XRF analysis also shows a Ni/Co molar ratio close to 1/2 in the $NiCo_2O_4$ sample.

Fig. 2a shows the SEM images of the $NiCo_2O_4$ microflowers. The $NiCo_2O_4$ microflowers have a narrow size distribution of 6–10 μm. It can be observed that the $NiCo_2O_4$ microflowers present an intriguing 3D structure of high hierarchy. The $NiCo_2O_4$ hierarchical microflowers are composed of $NiCo_2O_4$ nanoneedle bundles. Without the addition of nickel sources in the reaction solution, the Co_3O_4 was prepared and

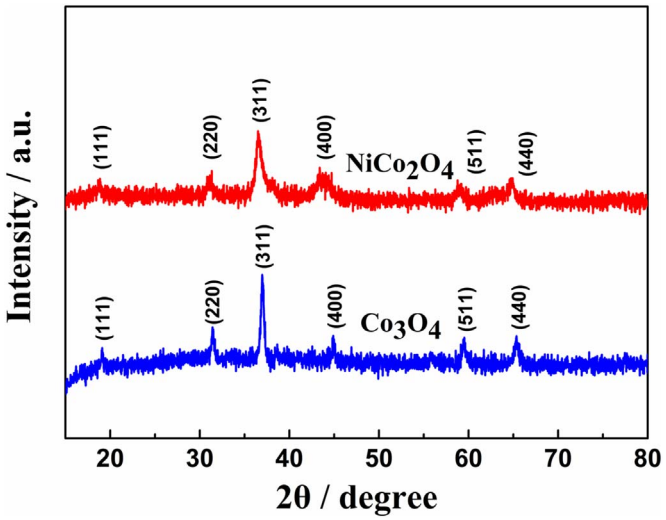

Fig. 1. XRD patterns of the Co_3O_4 and $NiCo_2O_4$.

exhibited a 2D sheet structure with high porosity (Fig. S1). The TEM image (Fig. 2b) of the $NiCo_2O_4$ microflowers clearly shows the $NiCo_2O_4$ nanoneedle bundles. The HRTEM image (Fig. 2c) of the $NiCo_2O_4$ nanoneedle presents clear lattice fringes, which conforms the high crystallinity of the $NiCo_2O_4$. The interplane spacing of 0.47 and 0.25 nm correspond to the (111) and (311) planes of $NiCo_2O_4$, respectively. EDS elemental mapping analysis (Fig. 2d) shows the homogeneous distribution of Co, Ni and O elements throughout the $NiCo_2O_4$ microflowers. These results again evidence the formation of the $NiCo_2O_4$. Fig. S2 shows the N_2 adsorption-desorption isotherm of the $NiCo_2O_4$ microflowers and the Co_3O_4 nanosheets. Both isotherms can be categorized as the type IV isotherm with a typical hysteresis loop. This indicates the mesoporous structure, which is consistent with the SEM and TEM observations. The Brunauer-Emmett-Teller (BET) surface area of the $NiCo_2O_4$ microflowers is calculated to be 37.6 $m^2\,g^{-1}$, which is more than 2 times higher than that (11.7 $m^2\,g^{-1}$) of the Co_3O_4 nanosheets. In addition, the average pore sizes of the $NiCo_2O_4$ and Co_3O_4 measured from the desorption branch with the Barrett-Joyner-Halenda (BJH) model are 17.6 and 30.5 nm, respectively. Such a mesoporous 3D architecture with large surface area and abundant pore channels is expected to endow the $NiCo_2O_4$ microflowers a good catalytic performance for the selective oxidation of styrene.

3.2. Catalytic performance

The oxidation of styrene using TBHP as the oxidant was carried out to assess the catalytic properties of the $NiCo_2O_4$ microflowers. For comparison, the catalytic properties of the Co_3O_4 nanosheets prepared by the same method as preparing the $NiCo_2O_4$ microflowers were studied. The molar ratio of TBHP and styrene is 5:1. GC analysis showed that the catalytic oxidation of styrene produced two major products, i.e. SO and benzaldehyde. Fig. S3a–c show the activity and selectivity of the SOR using Co_3O_4 and $NiCo_2O_4$ catalysts at 80 °C within 6 h. The Co_3O_4 nanosheets offered a selectivity of 62% to SO with a total styrene conversion of 53% at 6 h. In sharp contrast, the $NiCo_2O_4$ microflowers presented a much higher catalytic performance with a styrene conversion of 99% and a selectivity of 80% to SO. The overall SO yield of the $NiCo_2O_4$ catalyst (Fig. 3) is as high as 79%, which is more than 2 times that of the Co_3O_4 catalyst (33%).

To optimize the reaction conditions of the $NiCo_2O_4$ catalyst, the effects of the key reaction parameters (e.g., reaction temperature, styrene/TBHP ratio and reaction time) on SOR were investigated. Fig. S3c shows the effect of reaction temperature on the catalytic performance. Both selectivity to SO and styrene conversion show a volcano-