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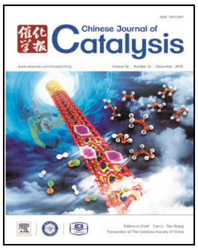

Article

Hierarchical 0D/2D Co_3O_4 hybrids rich in oxygen vacancies as catalysts towards styrene epoxidation reaction

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ABSTRACT

Great efforts have been devoted to the developing of simple, efficient and stable heterogeneous catalysts for the styrene epoxidation reaction (SER). Metal oxides can be of industrial importance by offering an economic and green route for selectively converting styrene into styrene oxide (SO). Herein, by treating the pristine porous 2D Co_3O_4 sheets with $NaBH_4$ solution, a novel hierarchical structure, *i.e.*, 0D Co_3O_4 nanoparticles decorated on 2D porous Co_3O_4 sheets, was obtained. This simple solution reduction strategy not only realizes the morphology evolution, but also induces the modification of the valence states of metal ions and the simultaneous generation of surface oxygen vacancies. The hierarchical 0D/2D Co_3O_4 hybrids rich in oxygen vacancies (OV-Co_3O_4) exhibit a much better SER performance than the Co_3O_4 sheets (P-Co_3O_4), with the yield of SO more than doubled. The excellent catalytic performance of the OV-Co_3O_4 can be ascribed to the synergistic effects regarding the hierarchical porous structure, the modification of surface chemical composition and the creation of surface oxygen vacancies.

1. Introduction

The catalytic oxidation of hydrocarbons is a very important reaction in the chemical industry [1–5]. Among the various oxidation reactions, the catalytic epoxidation of alkenes has aroused much attention in recent years both academically and industrially since epoxide products are vital intermediates in pharmaceutical industrials and production of fine chemicals [6–12]. Styrene oxide (SO), as an important epoxide, is widely used in the manufacture of bulk chemicals, surface coatings, cosmetics and epoxy resins, *etc.* [13–15]. The traditional way for synthesis of SO involves the dehydrochlorination of styrene chlorohydrin or the oxidation of styrene with organic peracids [16]. However, both methods suffer from several drawbacks such as using hazardous chemicals, generating a large amount of chemical wastes and showing poor selectivity for SO [16,17]. From the viewpoint of green and sustainable chemistry, these conventional methods have been replaced by the method involving H_2O_2, O_2 or organic hydroperoxides as sacrificial oxidizing agents.

Among the various homogeneous catalysts for the styrene epoxidation reaction (SER), cobalt ions and their complexes have been identified as more active ones [18–21]. However, the efficient separation and subsequent recycling of these homogeneous catalysts remains a big challenge and gives rise to environmental pollution, which severely limits their further application. Therefore, many heterogeneous catalysts, including cobalt-based catalysts, have been employed in the SER due to

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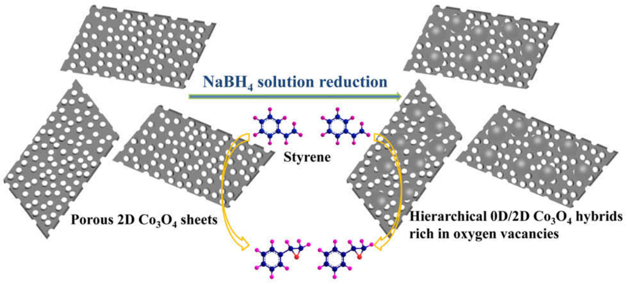
their mild reaction conditions and ease in catalyst separation and satisfactory recyclability [22–29]. Tang *et al.* [20,30] found that Co^{2+}-containing molecular sieves, mainly faujasite zeolite and MCM-41 exhibited better catalytic performance in the SER as compared with other transition metal (Cr^{3+}, Mn^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+})-containing counterparts. Li *et al.* [22] coated an ultrathin TiO$_2$ layer onto SBA-15 (TiO$_2$/SBA-15), and then introduced CoO$_x$ species on the support by atomic layer deposition. They reported that the 35CoO$_x$/5TiO$_2$/SBA-15 exhibited the best catalytic performance, showing 80.5% conversion with 67.5% selectivity to SO, which can be attributed to the appropriate interaction between the CoO$_x$ species and support. Moreover, Masunga *et al.* [31] prepared mesoporous manganese oxide, cobalt oxide, and hybrid Mn-Co oxide with an inverse surfactant micelle method. The results showed that the catalytic activities of the compared catalysts decreased in the order of Mn-Co_350>MnO$_2$_350> Co$_3$O$_4$_350, while the highest epoxide selectivity was achieved using MnO$_2$_350 (53.5%), and the recyclability test indicated that the metal oxides were stable with the structure well retained. Weerakkody *et al.* [32] further synthesized mesoporous Co$_3$O$_4$ by an inverse micelle template self-assembly method. They stated that high surface area, mesoporosity, and surface oxygen vacancies could be identified as the major contributors to the catalytic activity. Despite the advantages of these heterogeneous catalysts, however, they generally required complex preparation processes and showed low catalytic activity and/or poor selectivity of SO. Therefore, developing simple but highly active and stable cobalt-based catalysts for the SER is still a challenging and interesting study.

In this work, we attempt to achieve high styrene conversion and epoxide selectivity by rationally designing hierarchical 0D/2D Co$_3$O$_4$ hybrids rich in oxygen vacancies. As illustrated in Scheme 1, the OV-Co$_3$O$_4$ catalyst was prepared by a facile NaBH$_4$ treatment of the pristine porous Co$_3$O$_4$ sheets. Although this solution reductive strategy has just been reported to be effective in the applications of water splitting [33], *p*-nitrophenol reduction [34], and lithium storage and electrocatalytic oxygen evolution [35], to the best of our knowledge, it is the first report regarding this kind of catalyst treatment for the application in the SER. This simple modification of the P-Co$_3$O$_4$ can endow the OV-Co$_3$O$_4$ several advantages for the SER, such as improved surface area, abundant active sites and numerous surface oxygen vacancies. As expected, the OV-Co$_3$O$_4$ exhibits a much better SER performance including higher reactivity and SO selectivity than the P-Co$_3$O$_4$. In addition, a possible reaction pathway for the selective synthesis of SO from the SER with the OV-Co$_3$O$_4$ as the catalyst was reasonably proposed.



Scheme 1. Schematic illustration of the facile synthesis of hierarchical 0D/2D Co$_3$O$_4$ hybrids for the selective oxidation of styrene.

2. Experimental

2.1. Catalyst preparation

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

The P-Co$_3$O$_4$ was prepared according to the method reported in our previous study with some modifications [36]. In a typical procedure, 1.9 g Co(NO$_3$)$_2$·6H$_2$O was firstly dissolved in 60 mL DI water, and then 1.0 g polyvinylpyrrolidone *K*30 was added to the solution under vigorous stirring for 1 h. After that, 1.6 g CO(NH$_2$)$_2$ was added into the above mixture and stirred for another 1 h. Subsequently, the resulting mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 8 h. Thereafter, the precipitate was filtered, washed with DI water and ethanol several times, and dried at 80 °C for 5 h. The sample was then annealed at 500 °C at a ramping rate of 2 °C/min for 2 h to obtain the P-Co$_3$O$_4$.

For the synthesis of OV-Co$_3$O$_4$, 0.2 g P-Co$_3$O$_4$ was added to 0.02 mol/L NaBH$_4$ solution. After this simple treatment, the sediment was filtered and washed with DI water and ethanol several times. Then, the sample was dried at 80 °C for 5 h, and thus the OV-Co$_3$O$_4$ was obtained.

2.2. Catalyst characterization

X-ray diffraction (XRD) analysis was conducted on a D8 Advance diffractometer with Cu K_α radiation. Raman spectra were obtained on a Renishaw inVia laser Raman spectrometer. The morphologies of the samples were analyzed 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-desorption isotherms were collected at –196 °C on a Quantachrome Autosorb-iQ3. The X-ray photoelectron spectroscopy (XPS) data were obtained on a Thermo, Fisher Scientific ESCALAB 250Xi spectrometer.

2.3. Catalyst test

The obtained catalysts were applied for the SER in a round bottom flask equipped with a reflux condenser. In a typical process, 15 mmol of styrene and 75 mmol of tert-Butyl hydroperoxide (TBHP) were added to a mixture of 0.1 g of catalyst and 16 mL of acetonitrile in the flask placed in a water bath. During the test, the reaction mixture was sampled once an hour. After centrifugation, the products were analyzed by a gas chromatography equipped with a KB-1 column.

3. Results and discussion