

Synthesis of acetophenone from aerobic catalytic oxidation of ethylbenzene over Ti–Zr–Co alloy catalyst: Influence of annealing conditions

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ARTICLE INFO

Article history:

Received 10 October 2015

Received in revised form 1 December 2015

Accepted 7 December 2015

Available online 8 December 2015

Keywords:

Aerobic oxidation

Ethylbenzene

Ti–Zr–Co alloy

Anneal

ABSTRACT

The aerobic catalytic oxidation of ethylbenzene to produce acetophenone over an effective and robust heterogeneous Ti–Zr–Co has been studied. Under the optimum conditions, a high selectivity of 69.2% to acetophenone was obtained at a 61.9% conversion of ethylbenzene over Ti–Zr–Co catalyst, which is much better than the most results reported with heterogeneous catalysts. The catalytic performance and the active species of Ti–Zr–Co catalyst were discussed based on the changes of conversion and selectivity with varying the annealing temperature and atmosphere. It is confirmed that the surface CoO, Co₃O₄ species are the active sites, and the bulk structure of the alloy, CoTi₂ phase also present a large effect on the catalytic activity in present oxidation. As a cheap, robust and separable catalyst as well as a green oxidant is used, the present work provides a facile and green catalytic process for the oxidation of hydrocarbons.

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1. Introduction

The selective oxidation of hydrocarbon is of great importance in petrochemical industry for that it can transform petroleum feedstocks such as alkanes, olefins, and aromatics into a plenty of valuable organic chemicals, which are widely used in the preparation of polymer materials and fine chemicals etc. [1]. Generally, the oxidants such as *tert*-butylhydroperoxide, hydrogen peroxide, nitric acid, halides or ozone, etc. are used for the catalytic oxidation of hydrocarbons [2–6]. However, from the points of industrial application, these oxidants are expensive and un-environmentally benign such as *tert*-butylhydroperoxide, nitric acid and halides will leave large volume of organic waste, and hydrogen peroxide decomposes easily into water which will reduce the activity of the catalyst [7]. In term of eco-friendly sustainability, molecular oxygen is an ideal terminal oxidant, as it is much cheaper and more envi-

ronmental benign compared to the chemical oxidants mentioned above. Therefore, the aerobic catalytic oxidation is an important and green chemical process for the chemical industrial fabrication and it has attracted more attention in these years. Some effective catalysts have been developed for aerobic catalytic oxidation. For example, MnCP@SiO₂ catalyst was studied for the aerobic selective oxidation of ethylbenzene, in which the conversion of ethylbenzene was 22.9% and the selectivity of acetophenone reached to 74.9% at 100 °C [8]. Jin et al. reported a catalyst of hierarchically porous aluminophosphate-based zeolite with AEL and AFI structures, with it a 77.9% selectivity to acetophenone was obtained at a 14.8% conversion of ethylbenzene at 140 °C, 3 MPa O₂ in the absence of solvent [9]. Most recently, the non-metal catalyst is of high popular in the hydrocarbon oxidation, Luo et al. reported that carbon nanotubes were effective for the selective oxidation of ethylbenzene, the selectivity of acetophenone reached to 60.9% at a conversion of 38.2% at 155 °C, 1.5 MPa in CH₃CN [10]. Gao et al. reported that N-doped materials were active for the oxidation of hydrocarbons and alcohols [11]. In addition, they developed an effective palladium catalyst of Pd@N-doped carbon for the aerobic selective oxidation of ethylbenzene, in which the conversion of ethylbenzene was 14.2% and the selectivity of acetophenone reached up to 94% under

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atmosphere at 120 °C [12]. Chen et al. prepared Co–N–C/CeO₂ catalyst by a thermal annealing carbonization strategy, it exhibited a 74.8% selectivity to acetophenone at a 33.1% conversion for the ethylbenzene oxidation at 120 °C, 0.8 MPa O₂ [13].

The selective oxidation of ethylbenzene to acetophenone is an important reaction for that acetophenone is a very useful intermediate of the fine chemicals such as pharmaceuticals and perfume [14,15]. Usually, acetophenone is commercially produced from catalytic oxidation of ethylbenzene with molecular oxygen in the presence of homogeneous cobalt based catalyst and additives such as manganese and bromide species in an acetic acid solvent [16–18]. Herein, we will report an effective heterogeneous catalyst, Ti–Zr–Co metallic alloy, for production of acetophenone from oxidation of ethylbenzene with molecular oxygen. In our previous work, the Ti–Zr–Co alloy was found to be active and selective for the oxidation of cyclohexane, in which cyclohexanol and cyclohexanone were produced with a high selectivity of 90% at a conversion around 7% [19,20]. The Ti–Zr–Co catalyst is easy to handle and transport, simple and cheap in production, sturdy to wearing in the utilization, with comparing to those reported catalysts such as metal-organic complex, metal nanoparticles and nanocarbon materials. Therefore, it stimulates us to extend further study of the Ti–Zr–Co alloy catalyst in the aerobic catalytic oxidations. The catalyst showed a higher catalytic performance for the aerobic oxidation of ethylbenzene, in which acetophenone was produced as the main product with a selectivity of 69.2% at a 61.9% conversion, which are much better than the results reported in literature. The annealing temperature and atmosphere presented significant effects on the oxidation of ethylbenzene, after annealing at 450 °C in N₂ flow, the activity of Ti–Zr–Co increased significantly with a stable selectivity to acetophenone. The active species was discussed in detail by experimental data and the characterizations of the catalysts annealed under the different conditions. This study not only presents an effective and robust catalyst for the selective oxidation of ethylbenzene to acetophenone, but also gives a new insight into the effect of surface phase composition and bulk structure of Ti–Zr–Co alloy on the catalytic performance of aerobic oxidation.

2. Experimental

2.1. Ti–Zr–Co alloy preparation and characterization

Ti–Zr–Co catalyst was prepared by arc-melting of Ti (99 wt.%), Zr (97 wt.%) and Co (99 wt.%) metals with a mole ratio of 60:10:30 on a

water-cooled cuprum hearth in a high-purity argon atmosphere at 250 A. To make the chemical compositions homogenous, the alloy ingot was turned over and remelted at least three times. After that, the surface of the cast ingot was burnished in order to eliminate the oxide layer. Then the alloy ingot was crushed to powders by repeated manual beating with a steel pestle and mortar, and separated by 140 meshes screen, the powders with size smaller than 140 meshes (109 μm) were used for the reaction experiment. In some cases, the Ti–Zr–Co catalyst, before use, was annealed at 450 °C or 750 °C for 2 h under N₂ (denoted as Ti–Zr–Co-450-N₂ and Ti–Zr–Co-750-N₂) or at 450 °C for 2 h under air (denoted as Ti–Zr–Co-450-air) with a heating rate of 5 °C min⁻¹ in a tube furnace to obtain different treated Ti–Zr–Co catalysts. A CoTi₂ alloy was prepared by a method similar to the Ti–Zr–Co alloy catalyst as described above, except for without Zr involved. Co₃O₄ was purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China), is of analytical reagent. 7 wt.% Co₃O₄/TiO₂ was prepared according to literature [21].

The phase composition and microstructure of the alloys were examined by X-ray diffraction (XRD) on a Bruker-AXS D8 ADVANCE with Kα. The leaching of Ti, Zr or Co in the filtrate was not detected by ICP-OES measurement (iCAP6300, Thermo USA). XPS measurement was performed by using a VG Microtech 3000 Multilab, and the spectra of Co 2p, Zr 3d, Ti 2p, O 1s and C 1s were recorded, which were corrected to the C 1s peak at 284.6 eV. Scanning electron microscopy (SEM) image was performed on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 10 kV, and the size of particles was in a range of 50–100 μm (Fig. S1).

2.2. Ethylbenzene oxidation

Ethylbenzene and acetonitrile purchased from Beijing chemical plant are of analytical grade, and used without further purification, gas of O₂ (99.99%) (Changchun Xinxing Gas Company) is used as delivered. Typically, ethylbenzene (5 mL), acetonitrile (5 mL) and the Ti–Zr–Co catalyst (20 mg) were charged into a stainless steel autoclave with a Teflon inner liner (50 mL) at room temperature, then the reactor was sealed and preheated in an oil bath, after the reactor was heated up to the desired temperature, O₂ (2 MPa) was introduced and the reaction was started with a continuously stirring at 1200 rpm, and the reaction time was recorded. When the reaction finished, the reactor was cooled to room temperature and then depressurized carefully. The solid catalyst was separated

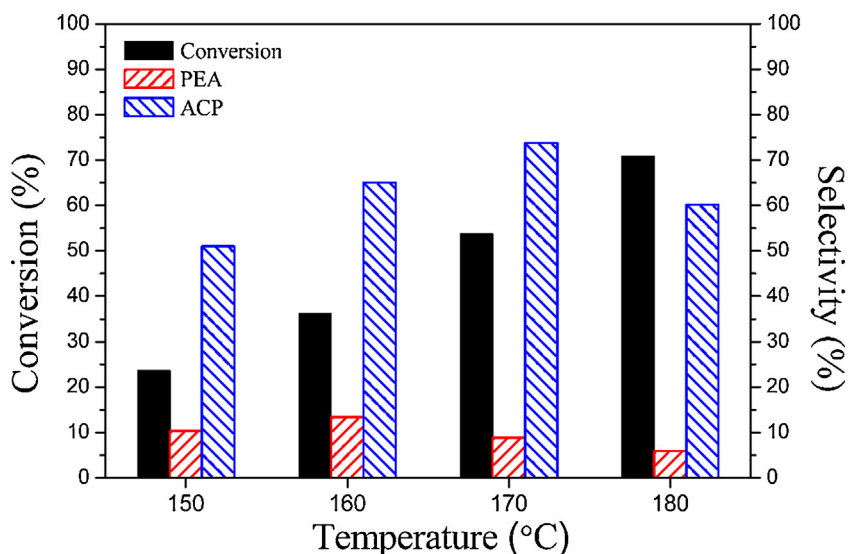


Fig. 1. The effect of temperature on the oxidation of ethylbenzene. Reaction conditions: 5 mL ethylbenzene, 5 mL CH₃CN, 20 mg Ti–Zr–Co alloy catalyst, 2 MPa O₂, 3 h.

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