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Efficient oxidation of ethylbenzene catalyzed by cobalt zeolitic imidazolate framework ZIF-67 and NHPI

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Abstract

Efficient catalytic oxidation of ethylbenzene to acetophenone was realized using the catalytic system of cobalt zeolitic imidazolate framework ZIF-67/N-hydroxyphthalimide (NHPI) under mild conditions. 95.2% conversion of ethylbenzene with 90.3% selectivity to acetophenone could be obtained at 373 K under 0.3 MPa O_2 for 9 h. The results show that there exists synergetic effect between ZIF-67 and NHPI. 1-Phenylethyl hydroperoxide (PEHP) was generated via a radical process involving the hydrogen abstraction from ethylbenzene by phthalimide N-oxyl, and subsequently effectively decomposed to acetophenone by ZIF-67.

Key words

N-hydroxyphthalimide; ZIF-67; oxidation; ethylbenzene; acetophenone

1. Introduction

With the rapid depletion of fossil energy resources and the increasing concerns of global environmental pollution, efficient and eco-friendly petrochemical production processes need to be explored. One possible strategy is to produce fine chemicals via the selective oxidation of aromatic hydrocarbons, including ethylbenzene, toluene and xylene isomers, etc. In recent years, the catalytic oxidation of ethylbenzene to acetophenone with molecular oxygen has drawn much attention in petrochemical industry [1−3]. Acetophenone is an important chemical and intermediate in medicine, spices, solvents and plastic plasticizers. With the rapid development of chemical industry, the demand of acetophenone is increasing. Molecular oxygen has been considered as a green and cheap oxidant, but it exhibits a triplet ground state, for which the oxidation of hydrocarbons in singlet state is spin-forbidden. Thus to realize the selective oxidation of ethylbenzene with molecular oxygen under mild conditions is still a challenge [4]. As we known, Ishii system combining NHPI with a variable valence metal, most of Co^{2+}, exhibited high efficiency in the oxidation of a wide range of hydrocarbons, such as cyclohexane, ethylbenzene and toluene [5]. However, the usage of acetic acid may cause corrosion to equipment and generates slagging. So developing new environmental friendly and efficient catalyst for catalytic oxidation of ethylbenzene to acetophenone is of great significance.

Metal-organic frameworks (MOFs) showed excellent catalytic performance in hydrocarbon oxidation [6]. Corma et al. [7] reported the combination of MOFs materials [Cu(2-pymo)$_2$] and [Co(PhIM)$_2$] as efficient catalyst for tetrahydronaphthalene oxidation. Cobalt(II)-containing metal-organic framework MFU-1 exhibited good catalytic activity in cyclohexane oxidation, in which the skeleton Co(II) was proposed as the redox activity site [8]. Recently, zeolitic imidazolate frameworks (ZIFs), as a new type of MOF material, have drawn much attention. It is formed through the complexation of N atom on the imidazole ring with divalent transition metal ions to possess zeolite topology. ZIFs combine the advantages of zeolite and traditional MOFs materials with high thermal stability, resistance to hot alkali and organic solvent, high porosity and large specific surface area.

We have focused on the synthesis of various functional materials and their catalytic performance in selective oxidation reactions of aromatic compounds [9−15]. In our previous

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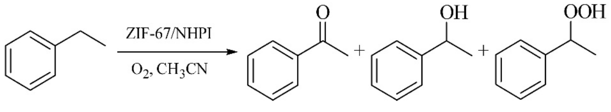
work, tetrahedral coordinated Co(II)O dispersed on SBA-15 showed much higher activity than cobalt acetate or Co_3O_4 in the liquid-phase aerobic oxidation of ethylbenzene [9]. Moreover, in our designed N-heteroaromatic ring containing N-hydroxy compound-based systems, the catalytic performance was remarkably improved by enhancing the efficiency in alkyl peroxide decomposition [12−14]. Considering that the redox zeolitic imidazolate framework ZIF-67 possesses the tetrahedral coordinated Co(II), we chose it to combine with NHPI as the catalytic system for the oxidation of ethylbenzene to acetophenone (Scheme 1).



Scheme 1. Oxidation of ethylbenzene catalyzed by ZIF-67/NHPI

2. Experimental

2.1. Chemicals and reagents

All the chemicals and reagents were of analytical grade, obtained from commercial sources, and used as received unless otherwise stated. Methanol, cobalt acetate hexahydrate, ethanol and acetonitrile were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. 2-Methylimidazole was supplied from Aladdin Industrial Corporation. Ethylbenzene was purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of ZIF-67

According to the literature, ZIF-67 was synthesized using colloid chemical method with minor modification [16]. A solution of 2-methylimidazole (6.489 g, 79.04 mmol) in 200 mL methanol was rapidly poured into a solution of $Co(NO_3)_2\cdot 6H_2O$ (2.933 g, 10.01 mmol) in 200 mL methanol under stirring for 8 h with a magnetic bar. The mixture slowly turned turbid, and the nanocrystals were separated from the milky dispersion by centrifugation at 8500 rpm followed by washing with fresh methanol. The nanocrystals were dried in vacuum (10^{-6} bar) at 80 °C in air.

2.3. Catalyst characterization

Nitrogen adsorption-desorption isotherms at liquid nitrogen temperature (–196 °C) were measured using Autosorb-1 (Quantachrome). All the samples were outgassed in vacuum at 130 °C for 3 h prior to measurement. The total surface areas were calculated according to the BET method. TEM images were recorded on JEOL-JEM-2000EX with samples deposited on a carbon support film. Scanning electron microscopy (SEM) was performed using a JSM-7800F electron microscope (JEOL). XRD patterns were obtained on a Rigaku D/Max-2500/PC powder diffraction system equipped with a Cu K_α radiation source ($\lambda = 0.15418$ nm) operating at 30 mA and 40 kV. Fourier transform infrared (FT-IR) spectra were conducted on a Bruker Tensor27 FT-IR spectrometer in the absorbance mode with a resolution of 4 cm^{-1}. Thermal gravity analysis (TGA) measurements were carried out on a NETZSCH STA 409 PC instrument. UV-Visible diffuse reflectance spectra of powdered catalyst were recorded between 190 and 900 nm on a Shimadzu 2450 UV-Visible spectrometer equipped with an integration sphere. Real-time in situ infrared spectroscopy measurements were carried out on a Mettler toledo ReactIRTM 45 m equipped with an Infrared Associates liquid nitrogen-cooled AgX fiber conduit diamond ATR probe.

2.4. Catalytic oxidation of ethylbenzene

Ethylbenzene oxidation experiment was preceded in a 50 mL autoclave. Typical operation process was as follows: 2 mL ethylbenzene and 10 mL acetonitrile were added into the autoclave containing 0.27 g NHPI and specified amount of ZIF-67. After heating to the specified temperature, 0.3 MPa O_2 was charged and constantly replenished in the process of reaction to keep O_2 pressure at 0.3 MPa. The reaction was stopped after 9 h, and the products were analyzed by gas chromatograph.

3. Results and discussion

3.1. Catalyst characterization

The as-synthesized sample was characterized by TEM, SEM, XRD, FT-IR, TGA and UV-Vis DRS spectra, and confirmed to be ZIF-67. As shown in Figure 1, TEM and SEM images revealed that the as-synthesized sample was polyhedral shaped crystals with smooth surface, which is similar to the literatures [17,18]. The average diameter was 265 nm and ranged from 100 to 500 nm from the analysis of TEM image. The sharp characteristic peaks in X-ray diffraction (XRD)

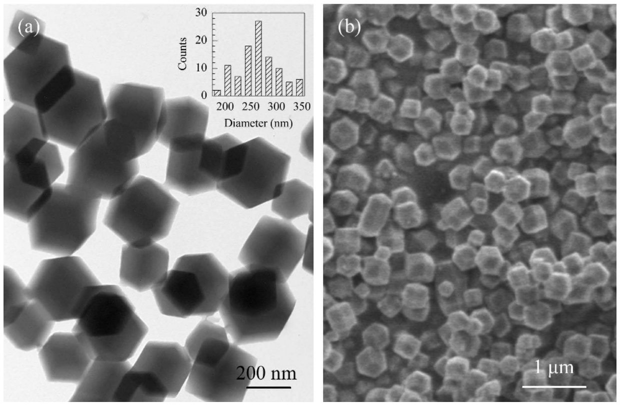


Figure 1. TEM image (a), particle size distribution (insert) and SEM image (b) of ZIF-67