Inorganica Chimica Acta 419 (2014) 66–72

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Epoxidation of styrene using carbon nanotubes-supported cobalt catalysts

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ARTICLE INFO

Article history:
Received 6 November 2013
Received in revised form 4 May 2014
Accepted 6 May 2014
Available online 14 May 2014

Keywords:
Epoxidation
Styrene
Carbon nanotubes
Cobalt catalysts

ABSTRACT

Cobalt supported on carbon nanotubes (Co/CNTs) was developed as a novel cost-effective catalyst by impregnating CNTs in metallic precursor solution. The structures of the Co/CNTs catalysts were extensively characterized, and the presence of nanometer-sized Co particles was confirmed. The activity of Co/CNTs catalysts were examined for the epoxidation of styrene with *tert*-butyl hydroperoxide (TBHP) as the oxidant. The results showed that the catalytic behavior of Co/CNTs catalysts was closely correlated with the nature of oxidants, the structure of supports, and the polarity of the solvents. Compared with hydrogen peroxide, TBHP was a better oxidant for the epoxidation of styrene with the Co/CNTs catalyst, due to the lower dissociation energy. The favorable catalytic performance was obtained in acetonitrile solvent. The oxygen species with a radical nature activated by TBHP on the Co(II) site was proposed for the epoxidation reaction. This study also demonstrated that Co/CNTs catalysts were stable and could be reused without significant loss of activity.

1. Introduction

Carbon nanotubes (CNTs) have been broadly applied as catalyst supports in the past decade [1–3], due to the distinct advantages, such as high resistant to acid and base corrosion, ideal surface chemical flexibility, high surface area, and exceptional chemical and physical stability [4]. Various transition metals and complexes have been supported on the CNTs for liquid-phase (e.g. hydrogenation [5], hydroformylation [6], methanol oxidation [7]) and gas-phase reactions (e.g. Fischer–Tropsch process [8], ammonia decomposition reactions [9]). Recently, the application of the CNTs-supported catalyst to the epoxidation of alkene has obtained high interest, which is an important and essential reaction for organic synthesis [10]. The product epoxides have been widely used for making epoxy resins, paints, polymers, surfactants, and medicines. Epoxides also have high values in the asymmetric synthesis, since the carbon ring can be readily broken to produce 1, 2-functionalities with a high degree of regio- and stereo-control [11,12]. Salavati-Niasari et al. [13] achieved a 80.6% conversion of cyclohexene and 82.7% selectivity to epoxide using cobalt (Co) Schiff base complex anchored on CNTs. Moghadam et al. studied the catalytic behavior of tungsten hexacarbonyl ($W(CO)_6$) [14] and molybdenum hexacarbonyl ($Mo(CO)_6$) [15] supported on CNTs, and found the heterogeneous metal carbonyl catalysts had high stability and reusability in epoxidation without losing their catalytic activity. However, even though these findings illustrated that Schiff base and metal carbonyl catalysts were capable of catalyzing the epoxidation reactions, the preparation procedure for these catalysts was complicated and many organic reagents (dimethylformamide, tetrahydrofuran, thionyldichloride, etc.) were needed. Alternatively, several studies found that the CNTs-supported gold catalyst was active in the oxidation of styrene with relative good conversion and high epoxide selectivity, and CNTs was the preferred support to other carriers (e.g. active carbon, graphite, TiO_2, SiO_2 and Al_2O_3) [16–18]. But the costly gold catalyst prohibits large-scale applications. Thereby, it is critical to explore cost-effective metal catalysts for epoxidation of alkene.

Cobalt (Co) is an important component for a broad range of catalytic reactions, including Fischer–Tropsch synthesis [19], reforming of methane [20], toluene oxidation [21] and CNTs synthesis [22]. Various supported Co catalysts, including Co^{2+}-exchanged zeolites [23], Co-substituted mesoporous materials [24], cobalt supported on silica [25], and Co immobilized in metal organic framework [26] have been developed to enhance the epoxidation of alkene. Our group recently introduced Co into the mesoporous silica via the ultrasonic irradiation [27], and found that this novel catalyst had excellent styrene conversion and selectivity to benzaldehyde in the oxidation of styrene with hydrogen peroxide.

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http://dx.doi.org/10.1016/j.ica.2014.05.006
0020-1693/

The objective of this study was to develop CNTs-supported cobalt (Co/CNTs) catalyst for the production of fine chemicals in the liquid-phase reaction. The main advantage of this catalyst was the simple preparation using conventional impregnation method, without the requirement of organic Schiff-base ligand or organic additive. Epoxidation of styrene was selected as the typical liquid-phase reaction to examine the Co/CNTs catalysts. There were three tasks in this study. First, the physicochemical properties of Co/CNTs catalysts were characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). Second, the characteristics of Co/CNTs catalysts were extensively compared with different loaded metals, supports, oxidants and solvents. The styrene conversion and epoxide selectivity were determined for each catalyst. Third, the reusability of Co/CNTs was evaluated for the long-term catalytic reactions.

2. Experimental

2.1. Catalysts preparation

Multi-wall carbon nanotubes (CNTs) (purity: >95%; length: 0.5–2 μm; outer diameter: 30–50 nm; inner diameter: 5–12 nm; carboxyl content: 0.73 wt.%; specific surface area: 111 m^2/g, Chengdu Organic Chemicals Co., Ltd. China) were used as the support. Co/CNTs were prepared via the conventional impregnation method. The loading of Co was 10 wt.% unless otherwise stated. In a typical preparation process, 0.5 g of CNTs were dispersed in the aqueous solution containing 0.247 g of $Co(NO_3)_2 \cdot 6H_2O$. After impregnation at room temperature for 30 min, the mixture was subjected to sonication irradiated using an ultrasonic generator (KH3200DE, KunShanHeChang Ultrasonic Instrument Co., Ltd.). Aftermath, the paste was dried in vacuum at 60 °C for 12 h. Catalysts containing other metal ions M/CNTs (M = Fe, Ni, Ce, Y, La) were synthesized through the same procedure using the corresponding nitrate salts.

2.2. Catalytic epoxidation reactions

The catalytic reaction was carried out in a 50 ml two-necked round-bottomed glass flask connected to a reflux condenser and a thermometer. The temperature of the reaction vessel was maintained using a water bath. Tert-butyl hydroperoxide (TBHP) (aqueous solution 70 wt.%) and hydrogen peroxide (H_2O_2) (aqueous solution 30 wt.%) were compared as the oxidants. Five solvents with different dielectric constants were tested for the reaction: acetonitrile, *N*,*N*-dimethylformamide, acetone, methanol and isopropanol. Before the oxidation reaction, 0.05 g catalyst was mixed with 10 ml solvent, 10 mmol styrene, and 10 mmol TBHP. The mixture was then heated with stirring under reflux at the desired temperature for 6 h. After the reaction, the catalyst was removed using a hydrophobic membrane. The organic compounds were analyzed quantitatively using a gas chromatograph (GC7900, Shanghai Techcomp Instruments Co., Ltd.) equipped with a 5% diphenyl-95% dimethylpolysiloxane benzyl siloxane capillary column, and a flame ionization detector (FID). The product identification was conducted for the pure compound and the quantitative analyses were performed by considering the FID response factors for each compound.

The styrene conversion and the selectivity for product were calculated as followings:

$$\text{Conversion}(\%) = \frac{(\text{moles of initial styrene}) - (\text{moles of final styrene})}{(\text{moles of initial styrene})}$$

$$\text{Selectivity}(\%) = \frac{\text{moles of product formed}}{\text{moles of styrene consumed}} \times 100$$

2.3. Characterization

The surface chemical composition was performed using X-ray photoelectron spectroscopy (XPS) (Amicus, KRATOS) equipped with a standard Al Kα excitation source ($h\nu$ = 1486.6 eV). The binding energy was calibrated using C1s photoelectron peak at 284.6 eV as a reference. Photoemission data were collected and processed by using the CasaXPS (2.3.12Dev7) software. Surface morphology of the samples was examined by transmission electron microscopy (TEM) (JEM-2100HR, JEOL) equipped with LaB_6 electron gun and operated at an accelerating voltage of 200 kV. The samples were dispersed ultrasonically in ethanol and then deposited on a copper grid. The crystalline phases of the catalysts were measured by X-ray diffraction (XRD) (D8 Advance, BRUKER) with a Cu Kα (λ = 0.154 nm) radiation source. The tests were operated at 40 kV and 40 mA over the scattering angle of 2θ from 20° to 80° with a step size of 0.02° at an acquisition time of 0.1 s per step. Crystal phases were identified by the Joint Committee on Powder Diffraction Standards (JCPDS) files. In order to examine the Co leaching from the Co/CNTs catalyst, the concentration of Co ions in the reaction solution was evaluated by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Prodigy, Leeman).

The dissociation energy of TBHP and H_2O_2 by breaking one hydrogen atom was calculated based on GAUSSVIEW 5.0, using the density functional theory (DFT) at the level of B3LYP/6-31+G (d). Acetonitrile was chosen as the solvent in the built-up of the calculation model.

3. Results and discussion

3.1. Epoxidation of styrene using CNTs-supported metal catalysts with TBHP and H_2O_2 as oxidants

Catalysts with different metal elements had significant effects on the epoxidation of styrene. The catalytic performance in terms of the styrene conversion and the selectivity to epoxide and benzaldehyde with TBHP as the oxidant was determined (Fig. 1A). Iron, nickel, and other rare earth elements (yttrium, lanthanum, cerium) were chosen in this study, since these elements incorporated into mesoporous molecular sieves or hydrotalcites had been used as catalysts in the epoxidation of alkene [28–30]. The styrene conversions varied substantially with different metal species. Although Ni, Y, La-containing catalysts exhibited higher selectivity of benzaldehyde, their styrene conversion were lower. The main product with Fe, Co, Ce-containing catalysts was epoxide, and Co/CNTs showed the highest selectivity of epoxide (80%) with 38% conversion of styrene, which indicated that Co/CNTs were the most effective catalyst for the epoxidation of styrene. The difference in the catalytic performance was caused either by the different natures of metal element or by the coordination of the solvent to metal ions.

In addition, the type of oxidants affected the catalytic activity of styrene oxidation (Fig. 1B). The oxidation with TBHP had a higher conversion than that with H_2O_2. For both TBHP and H_2O_2, a radical chain mechanism became effective, and the hydroperoxy radical attacked the C=C double bonds to form the epoxide [11]. In order to understand the formation of hydroperoxy radicals, the dissociation energy of TBHP and H_2O_2 by breaking one hydrogen atom was calculated. The density functional theory (DFT) results showed that the dissociation energy was 341.7 kcal/mol for TBHP and 358.5 kcal/mol for H_2O_2, which indicated that the hydroperoxy radical formed by TBHP was easier than by H_2O_2, and TBHP was a more-efficient oxidant than H_2O_2. This calculation data were in