



Short communication

Direct oxidation of benzene with molecular oxygen in liquid phase catalysed by heterogeneous copper complexes encapsulated in Y-type zeolite



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ARTICLE INFO

Keywords:

Hydroxylation
Phenol production
Heterogeneous catalysis
Copper benzoate complexes
Oxygen oxidation

ABSTRACT

Liquid-phase direct catalytic oxidation of benzene to phenol was performed by using a copper complex in Faujasite-type zeolite with molecular oxygen as an oxidant and sucrose as a reducing agent. Heterogenisation of the copper complex was achieved by a ship-in-a-bottle method, which enabled the encapsulation of the copper complex in the supercages of a Faujasite-type zeolite. Heterogenisation also provided the catalyst, reactant and the product in separate phases result that allowed their facile separation. All the prepared copper complex-based catalysts exhibited high activity and reusability for the direct oxidation of benzene to phenol. Based on differential thermal analysis, thermogravimetry (DTA-TG) and X-ray absorption fine structure (XAFS) measurements, it was confirmed that the copper complex was encapsulated in the supercages of Y-zeolite. The formation of phenol over the copper complex encapsulated in Y-zeolite was also investigated by using sucrose in the aqueous solution of acetic acid. Sucrose was an effective additive as a reducing agent because it was hydrolysed into two reducing sugars, namely glucose and fructose, under the reaction conditions applied. Overall, this work provides a successful approach for the potential use of heterogeneous metal complex catalysts suitable for liquid-phase oxidation reactions with molecular oxygen.

1. Introduction

Phenol is one of the important chemical compounds in the fields of synthetic chemistry, petrochemicals and plastics, and it is employed as a chemical intermediate for the production of phenolic resins and other phenol derivatives. Almost 90% of phenol production throughout the world is based on the cumene process, which is an industrial process for producing phenol and acetone from benzene and propylene, respectively [1,2]. The cumene process consists of three steps and has several disadvantages, such as environmental burden, high-energy consumption and an explosive intermediate product – cumene hydroperoxide. Although there is a demand for acetone as a solvent, the demand for phenol is rising faster than that for acetone [1,3]. Thus, the attractive prospect of producing phenol from benzene by direct oxidation has received much attention [4–6].

Selective production of phenol through the direct insertion of oxygen into the C–H bond is a challenging method and has been studied by many researchers [7–11]. Previous works often describe the production of phenol using hydrogen peroxide and other oxidising reagents [12–14]. Presently, one challenge is the use of molecular oxygen for the direct oxidation, as an easily handled oxidising reagent with the least cost and danger. Molecular oxygen normally exists in a triplet

ground state, which can only proceed with chemical reactions with general substrate molecules in an excited singlet state by the spin-forbidden transition of the molecular oxygen from triplet to singlet [15]. For the selective oxidation of benzene with molecular oxygen, catalysts that can selectively activate molecular oxygen to form an excited singlet state of oxygen under mild conditions are desired [16]. We have already reported that a copper catalyst can enhance the direct formation of phenol from benzene using molecular oxygen in the liquid-phase [17,18]. Copper complexes are used in a wide range of oxidation reactions. However, the use of homogeneous metal complex catalysts is often associated with problems like high-energy consumption and high reuse cost. Therefore, immobilization of homogeneous catalysts on a solid support material has attracted much attention [19–21] because of their large potential industrial applications. Heterogeneous catalysts have a number of significant advantages over the homogeneous ones because the former is easily recoverable and reusable and generate minimum wastes. A large number of studies has been conducted on the heterogenisation of metal complexes, which still receive considerable attention [22,23]. In this study, the immobilization of copper complex catalysts by their encapsulation in the supercages of Y-zeolite was demonstrated. The encapsulated catalysts were characterised by X-ray diffraction (XRD), differential thermal analysis and thermogravimetry

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(DTA-TG), and X-ray absorption fine structure (XAFS) spectroscopy. Recycling catalytic tests for the liquid-phase oxidation of benzene to phenol showed their potential application as heterogeneous catalysts. Moreover, this study revealed that sucrose appears an alternative reducing agent of previously reported reagents.

2. Experimental

2.1. Materials

Benzene, sucrose, acetic acid, copper(II) acetate, picolinic acid (PA), 2-pyridine carbonic acid (PCA), and quinaldic acid (QA) were purchased from Nacalai Tesque. The faujasite-type zeolite, H-Y (Y-zeolite; Si/Al = 5.1) was obtained from ZEOLYST. All the reagents and solvents were used as received without further purification.

2.2. Catalyst preparation

Heterogeneous copper complexes were prepared by a ship-in-a-bottle method [19]. An aqueous solution of copper(II) acetate (100 mg, 0.50 mmol) was added to a suspension of Y-zeolite (3.00 g in 200 mL of ion exchanged water). The mixture was stirred magnetically in a 500 mL flat-bottom flask at 353 K for 48 h under reflux. The solid fraction was filtered off, thoroughly washed with 2 L of hot water and dried at 373 K overnight. The obtained solid, in which the copper ions were ion-exchanged, was designated as Cu–Y. The latter was then added to a solution containing a given ligand, e.g., picolinic acid, 2-pyridin carbonic acid and quinaldic acid, in 200 mL of methanol, stirred at 333 K for 20 h under reflux and then filtered off. The obtained solid was stirred in 200 mL of methanol at 333 K for 5 h under reflux to wash out the unreacted ligand. The final catalysts were obtained by filtering off the solid and drying it at 393 K overnight. The catalysts were designated as CuPA-Y, CuPCA-Y, and CuQA-Y, which have picolinic acid, 2-pyridin carbonic acid and quinaldic acid as the ligand, respectively.

As a reference sample, Y-zeolite supported with copper(II) oxide was prepared by an impregnation method. Briefly, 3.00 g of Y-zeolite and the prescribed amount of copper(II) acetate were added to 200 mL of ion exchanged water and thoroughly stirred at room temperature. The suspension was dehydrated in vacuum at 333 K. The obtained solid was calcined in air flow at 673 K for 5 h. The catalyst was designated as Cu/Y (Imp).

2.3. Catalytic performance test

Hydroxylation of benzene in the liquid phase was performed in a 200 mL pressure-proof Pyrex batch reactor. Benzene (5.6 mmol, as the substrate), the encapsulated copper complex catalyst (100 mg), sucrose (0.4 mmol, as a reducing reagent), and aqueous acetic acid solution (5 mL, 20 vol%) were charged into the reactor. The reactor was purged completely using 0.4 MPa of O₂ (gauge pressure). The reaction was initiated by placing the reactor in an oil bath at 353 K and stirring magnetically. After 20 h of reaction time, the reactor was cooled to room temperature. A solution of toluene (0.2 mL) and 2-propanol (5 mL) was added to the reaction solution as an internal standard. The mixture was centrifuged to recover the catalyst from the solution, and the recovered catalyst was thoroughly washed with acetone and dried at 393 K overnight. The liquid-phase products were analysed by a high-performance liquid chromatography (Jasco MD-2010 Plus equipped with a GH-C18 column). The gas-phase products were detected by a gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector and using stainless steel columns containing active carbon (1 m) and molecular sieves 13 × (3 m) at 323 K under H₂ carrier.

2.4. Catalyst characterisation

The copper content of the samples was measured by XRF (Rigaku Primini) equipped with Pd as the X-ray source. DTA-TG measurements were carried out in DTG-60 (SHIMAZU) to confirm the formation of copper complexes. The samples were heated up to 1173 K at the rate of 10 K/min in air for the DTA-TG measurements. The XRD measurements were recorded using a Rigaku RINT-2100 diffractometer (with Cu K α radiation and a graphite monochromator). Zeolite samples were analysed in the range of 5–40° 2theta with a step size of 0.02° and a scan speed of 4°/min. Cu K-edge X-ray absorption fine structure (XAFS) analysis was performed at the beamline BL01B1 of Spring-8. The pelletized sample was sealed in a polyethylene bag charged with nitrogen. Fourier transformation for the copper samples was performed on k³-weighted XAFS oscillations in the range of 3–12 Å⁻¹.

2.5. Computational methods

All theoretical calculations were performed using the Gaussian 03 program [24]. The structures of the copper complex catalysts were optimised using the density function theory (DFT) method at the B3LYP/LanL2DZ computational level [25–27]. The corresponding vibrational frequencies were also calculated at the same level.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the powder diffraction patterns of the copper complex encapsulated in the supercages of zeolite catalyst. The diffraction pattern of pure proton-type Y-zeolite is shown in Fig. 1(a). The XRD patterns of all the samples are in good agreement with those reported in the literature [28]. However, compared to that of pure Y-zeolite and Cu-Y, the diffraction peak intensity I_{220} assigned to the (220) crystal face is reduced in the case of CuPA-Y, CuQA-Y and CuPCA-Y solids. The I_{220} is higher than I_{311} in the case of proton-type Y-zeolite and Cu-Y, whereas it is lower than I_{311} in the case of CuPA-Y, CuQA-Y and CuPCA-Y. It has been reported that an empirically derived relationship exists between the (331), (311) and (220) XRD peak intensities and the cation location in the faujasite-type zeolites [29,30]. The change in the relative peak intensity between I_{220} and I_{311} suggests that copper complexes are formed (located) in the supercages of Y-zeolite [31].

3.2. DTA-TG analysis

DTA-TG analysis of CuPA-Y, CuQA-Y and CuPCA-Y solids, using the proton-type Y-zeolite as the reference, is provided in Fig. 2(a–c). Based on the DTA-TG curves of the proton-type Y-zeolite, it is clear the occurrence of a one-step of weight loss due to the desorption of water

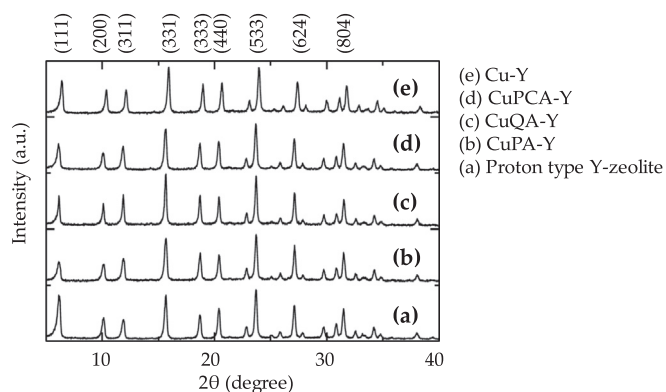


Fig. 1. XRD patterns of the proton type Y-zeolite and copper complex catalysts

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