



β -cyclodextrin grafted on lignin as inverse phase transfer catalyst for the oxidation of benzyl alcohol in H₂O



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ARTICLE INFO

Article history:

Received 7 December 2015

Received in revised form 15 February 2016

Accepted 16 February 2016

Available online 19 February 2016

Keywords:

β -CD
Lignin
Phase transfer catalyst
Synergistic effect
BzH

ABSTRACT

β -cyclodextrin grafted on lignin (β -CD) was prepared by the reaction of β -cyclodextrin (β -CD) and lignin with epichlorohydrin (EPI) as a cross-linking agent. The polymer was characterized by Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), Scanning electron microscopy (SEM), and solid-state nuclear magnetic resonance spectroscopy (CP-MAS-NMR). It was used as an inverse phase transfer catalyst for selective oxidation of benzyl alcohol (BzOH) to benzaldehyde (BzH) with hydrogen peroxide as the oxidant. The effects of various reaction variables, e.g., catalyst, the amount of catalyst, stirring speed, reaction temperature, oxidant, and cocatalyst on the catalytic performances were investigated. Under optimal conditions, high selectivity (>99%) was observed for the oxidation of BzOH under rather mild conditions. A plausible mechanism for the liquid-solid phase oxidation of BzOH has been proposed. Synergistic effects based on weak interactions between catalyst and support played an important role for the effective oxidation of BzOH under solution condition. The catalyst can be easily recycled and reused without a significant loss in reaction activity and selectivity, which would lead to its potential application foreground for environmental friendly synthesis of BzH.

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1. Introduction

Oxidation of alcohols to corresponding aldehydes has been widely concerned and researched. As a typical oxidation product of alcohol, benzaldehyde (BzH) is extensively used as a raw material in cosmetics, perfumery, food, and pharmaceutical industries.^{1–3} Commercially, it is produced from hydrolysis of benzal chloride or oxidation of toluene in liquid phase.^{4,5} However, traces amount of chlorine may be introduced in product for the former route and poor selectivity of BzH for the latter process. Currently, liquid phase oxidation of BzOH to BzH is a preferred synthetic route for it is eco-friendly and economically efficient.^{6,7} Hydrogen peroxide (H₂O₂) has been widely applied for oxidizing organic substrates due to its clean and environmentally friendly nature. Oxidation of BzOH by hydrogen peroxide or molecular oxygen in aqueous phase has been reported in combination with recyclable catalysts.^{8–11} Some metal-

catalyzed alcohol oxidations involve the use of homogeneous and heterogeneous catalysts, e.g., organometallic complexes,^{12,13} metal nanoparticles,^{14,15} and supported Pd,¹⁶ have been employed. In addition, Iron-chloride immobilized ionic liquid (SIL-FeCl₃) as a green heterogeneous catalyst was also used to prepare BzH from BzOH with excellent catalytic activity.¹⁷ However, most reported catalytic oxidation systems demonstrated some intrinsic drawbacks, including use of organic solvents, low selectivity due to over-oxidation of BzH, mass transfer limitation, environmental pollution, high cost, and difficulty to recover. From the viewpoint of economy and sustainable chemistry, developing a cheap and metal-free catalyst with high selectivity may be a better alternative to noble metal for the oxidation of BzOH.

Over the past few decades, supramolecular reactivity has attracted tremendous interests.^{18,19} As one of supramolecular hosts, cyclodextrins (CDs) have been introduced into the water-phase catalytic systems including oxidation, reduction, ring opening and hydrolysis etc.^{20–23} CDs are cyclic oligosaccharides composed of 6–8 glucopyranose units (namely α -, β - and γ -CDs) linked by glycosidic bonds.^{24,25} They have a torus structure with a hydrophilic

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exterior and a hydrophobic internal cavity. One of the striking features of CDs is that they can form inclusion complexes with different guest molecules in aqueous solution through host-guest interactions. They have also been employed as catalysts for chemical reactions.^{26,27} On the basis of economic criteria, ease of separation and recyclable utilization of the catalysts, the immobilization of CDs on solid supports is highly desirable. Immobilized CDs have gathered much attention in organic synthesis because they possessed some advantages such as high catalytic activity and easy recycling for the catalytic reaction compared with free CDs. They have been successfully introduced to catalyze some reactions.^{28–31}

With increasing concerns on environmental safety, the use of renewable sources and reduction of waste has attracted great concern worldwide. Lignin is the second most abundant natural resources after cellulose, and the major phenolic aromatic polymers in nature.³² The global production of lignin is more than 50 million tons per year, and about 95% of the output was disposed as a main by-product from pulp and paper industry due to its complex irregular macromolecular properties.³³ However, lignin is rich in hydroxyl groups arising from phenolic hydroxyl and carboxylic groups, and its graft polymerization with some monomers has been an effective way to introduce functional groups to improve its properties.^{34,35} Recently, a series of catalytic systems based on the synergistic effects between catalyst and support have been reported for the oxidation of substrates extensively.^{29,31}

Among CDs, β -CD is generally the most useful due to its appropriately sized cavity, accessibility, and lowest cost. In addition, β -CD contains a hydrophobic central cavity, which can form inclusion complexes with different guest molecules by noncovalent bonding in aqueous solution. It can be used to selectively catalyze chemical reactions by the weak interactions, which is extremely similar to the exact molecular recognition of an enzyme to a substrate.²⁹ In the present paper, β -CD grafted on lignin crosslinked by EPI as crosslinking agent (ι - β -CD) was first prepared and used as a recyclable heterogeneous catalyst for the oxidation of BzOH to BzH under mild reaction conditions. The obtained catalyst exhibited excellent catalytic activity for solution selective oxidation of BzOH and its structure was systematically characterized by various physico-chemical techniques. In addition, a rational mechanism of the oxidation was proposed.

2. Results and discussion

2.1. FTIR analysis

FTIR spectra of lignin (a), LE (b), β -CD (c), and ι - β -CD (d) are presented in Fig. 1. The FTIR spectrum of lignin displays the peaks ascribed to the O–H stretching vibrations (around 3440 cm^{-1}), C–H stretching of $-\text{CH}_3$, $-\text{CH}_2$ groups (around 2950 – 2835 cm^{-1}), C=O stretching vibrations of ketone group (around 1700 – 1560 cm^{-1}), and the peaks at 1590 , 1514 , and 1410 cm^{-1} assigned to the stretching vibrations of the C–C bonds in the aromatic skeleton. Peaks at 1375 , 1265 , and 1220 cm^{-1} due to the stretching vibrations of C–O are also observed. These results are in agreement with previously reported data.³⁷ The characteristic bands associated with the presence of specific functional groups of β -CD have been identified and described in the previous publications.^{38,39} The FTIR spectrum of ι - β -CD is similar to those of lignin and β -CD, indicating that their frameworks are not changed. The peaks of ι - β -CD at 3440 and 1030 cm^{-1} are stronger than those of β -CD. The increased intensity may be attributed to the presence of more $-\text{OH}$ and C–O–C groups in ι - β -CD. The peak at 916 cm^{-1} due to the epoxy ring of LE is completely disappeared (Fig. 1b), indicating the complete consumption of the epoxy groups due to the polymerization reaction.⁴⁰ The band at 837 cm^{-1} due to C–H in-plane deformations in aromatic rings is observed for both ι - β -CD

and lignin, which shows the aromatic nature of the samples.⁴¹ Thus, it can be concluded from the FTIR spectra that β -CD has been grafted on the surface of lignin successfully.

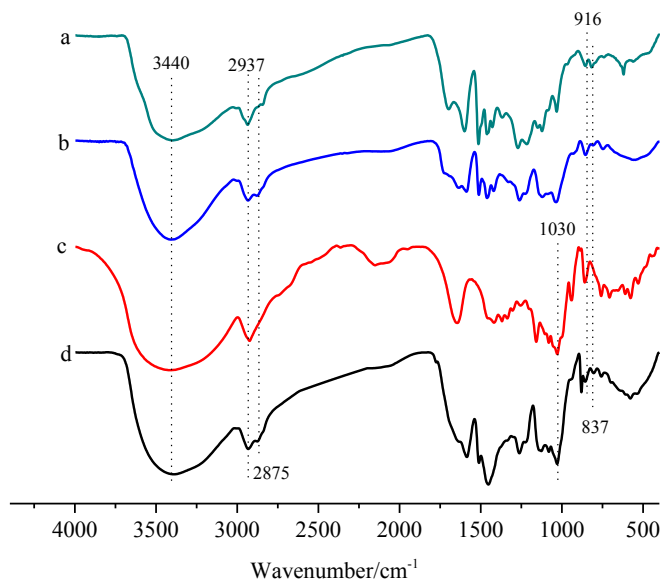


Fig. 1. FTIR spectra of lignin (a), LE (b), β -CD (c), and ι - β -CD (d).

2.2. TG analysis

TG curves of lignin (a), LE (b), and ι - β -CD (c) were shown in Fig. 2. Two weight losses were observed for lignin in the TG curve (Fig. 2a). The first weight loss was about 2.3% from 30 to $150\text{ }^\circ\text{C}$, which was caused by dehydration. The second stage started at about $200\text{ }^\circ\text{C}$ with weight loss of 40.5% due to heat decomposition of lignin. For the TG curve of LE, the weight loss of about 6.3% before $150\text{ }^\circ\text{C}$ was due to evaporation of water in the sample, and the second weight loss of about 49.6% was attributed to the thermal cleavage of LE (Fig. 2b). As for ι - β -CD, the weight loss before $150\text{ }^\circ\text{C}$ was about 5.1% due to the evaporation of the adsorbed water on the surface of ι - β -CD and the included water in the cavity of β -CD. In the range of 150 – $550\text{ }^\circ\text{C}$, the second weight loss of ι - β -CD was about 49.6% (Fig. 2c). Thus, the amount of β -CD grafted on the surface of lignin is about 6% (m/m). In addition, the second

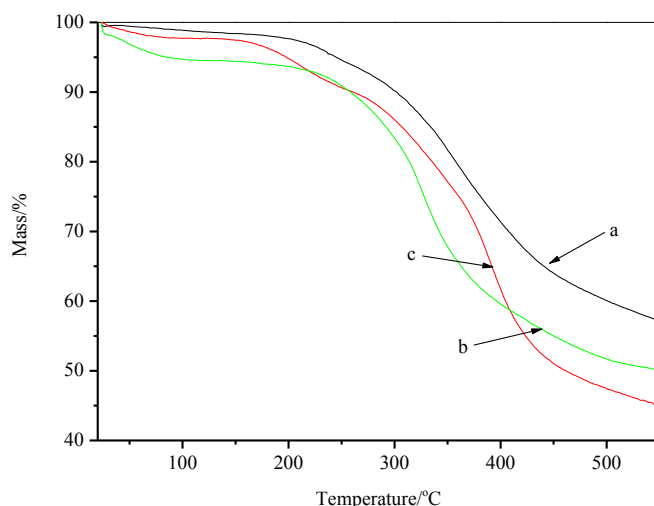


Fig. 2. TG profiles of lignin (a), LE (b), and ι - β -CD (c).

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