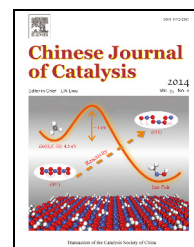


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Article

Synergistic effect of hydrogen bonding mediated selective synthesis of benzaldehyde in water

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ABSTRACT

β -cyclodextrin-functionalized cellulose was prepared from cellulose and β -cyclodextrin crosslinked with epichlorohydrin. The supramolecular polymer has been used as a heterogeneous catalyst for the synthesis of benzaldehyde under mild reaction conditions with high activity and yield. The catalyst was easily recovered and reused without significant activity loss. The β -cyclodextrin in the polymer formed host-guest complexes with cinnamaldehyde via noncovalent bonding. In addition, multiple interactions were observed between β -cyclodextrin and the substrate via intermolecular O–H...O hydrogen bonding. The significant promotion for the catalytic performance could be attributed to the synergistic effects of hydrogen bonding.

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1. Introduction

Hydrogen bonding is one of the most important interactions encountered in the gas, liquid and solid states. It plays a key role in mediating many chemical, physical and biochemical processes [1–3]. It is a bond between an electron-deficient hydrogen and a region of high electron density [4,5], typically between a hydrogen atom attached to either O or N and another electronegative atom such as F, N or O. Recently, hydrogen-bond-mediated catalytic processes have been studied extensively and several outstanding reviews have been published [6–8].

β -cyclodextrin (β -CD) is a cyclic oligosaccharide consisting of seven D-glucopyranose units linked by α -(1-4) glycosidic bonds to form a torus-shape with an inner hydrophobic and outer hydrophilic structure. It can efficiently accommodate a

wide variety of compounds in the cavity to form inclusion complexes in solution or in the solid state [9,10]. The selective association of target molecules by β -CD is extremely similar to the molecular recognition of a substrate by an enzyme. β -CD has been used to catalyze a number of chemical reactions via non-covalent bonding, and has demonstrated enzyme-like specificity and selectivity [11–13]. Recent reports have indicated that the presence of hydrogen bonds between β -CD and the substrate results in a significant improvement in the reaction selectivity [14–16]. However, β -CD is not a good model for enzyme catalysis because β -CD has limited catalytic activity due to the weak intermolecular interactions between β -CD and the substrate. If the catalytic site could have the synergistic effects of more functional groups, recognition should be more precise, and more like what is seen in enzyme recognition [17–19]. But

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to the best of our knowledge, β -CD derivatives based on the synergistic effects of multiple hydrogen bonds have not been applied to organic reactions, despite some reports on the acceleration of reaction rates and obvious enhancements in selectivity [20–22].

In the present study, β -cyclodextrin-functionalized cellulose polymer (β -CDCP) has been developed to investigate the production of natural benzaldehyde under mild conditions by the synergistic effects of additional weak interactions e.g. hydrogen-bonding between the polymer and the substrate (Scheme 1). Various physical chemistry techniques have been used to characterize the structure of the polymer. Density functional theory (DFT), a useful technique to define the host-guest interactions and the catalytic mechanism, has been employed to investigate the nature of the inclusion process on the reaction. Additionally, a plausible oxidation mechanism has been proposed based on XPS, FTIR and other experimental results.

2. Experimental and computational section

2.1. Preparation of β -CDCP

β -CDCP was synthesized by reacting β -CD with epichlorohydrin cross-linked cellulose in a NaOH solution according to a procedure reported earlier with some modifications [23]. 2 g of cellulose was dispersed in 30 mL of 25% NaOH solution. 7 mL of epichlorohydrin was then added dropwise to the mixture. The mixture was further stirred at 40 °C for 4 h. Subsequently, the intermediate was filtered, washed by acetone and water to remove epichlorohydrin thoroughly, and then centrifuged and rinsed with water to remove any residual NaOH and any water-soluble impurities until the pH of the supernatant approached neutral. The intermediate was dried under vacuum at 40 °C for 12 h to obtain epichlorohydrin modified cellulose (CE).

2 g CE dispersed in 30 mL NaOH solution (25%) was mixed with 0.7 g of β -CD, and the mixture was stirred at 40 °C for 6 h. The solid product was separated by centrifugation and washed until neutral with distilled water. Finally, it was dried at 60 °C for 24 h under vacuum. The amount of β -CD immobilized on the cellulose was determined to be 0.146 mmol/g by the previously reported method [24].

2.2. Preparation of the inclusion complex of cinnamaldehyde with β -CDCP

β -CDCP was completely dispersed in 25 mL deionized water. An equimolar amount of cinnamaldehyde was then added. The solution was stirred at 25 °C and 250 r/min for 1 h, and then centrifuged. The resultant solid was washed with distilled water to remove any residual substrate, and dried at 50 °C for

12 h under vacuum. The product was stored in a desiccator before use.

2.3. Characterization of β -CDCP and its inclusion complex

FTIR spectra (400–4000 cm^{-1}) were recorded on a Bruker TENSOR 37 FT-IR spectrometer. XPS spectra were measured on a Vacuum Generator ESCALAB 250 spectrometer with an Al $K\alpha$ monochromatic X-ray source and a hemispherical analyzer. A fixed analyzer pass energy of 150 eV was used for the survey scans, and high-resolution scans of core-level regions were recorded using a 20 eV pass energy. All core-level spectra were referenced to the C1s neutral carbon peak at 284.5 eV and obtained at a takeoff at 90° to the sample surface.

2.4. General procedure for oxidation of cinnamaldehyde

1 mmol of cinnamaldehyde was dissolved in 25 mL of deionized water at 70 °C in a 100 mL three-necked flask equipped with a reflux condenser and electromagnetic stirrer. 1 g of β -CDCP was then added and the mixture was stirred for 30 min. 2 mmol of NaHCO_3 dissolved in 4 mL of 30% H_2O_2 was slowly added dropwise. The mixture was stirred at 70 °C for 3 h, and then extracted with ethyl acetate and centrifuged. The organic phase was analyzed by GC-MS with naphthalene as an internal standard. The data were reproducible to within 5%.

2.5. Kinetic experiments

Cinnamaldehyde (1 mmol) was dissolved in 100 mL of deionized water in a 100 mL three-necked flask equipped with a reflux condenser and magnetic stirrer, before 0.5 g of β -CDCP was added. The mixtures were heated to reaction temperature (30, 40, 50 or 60 °C) and stirred for 30 min. Then, 2 mL of 30% H_2O_2 and 1.5 mmol of NaHCO_3 were added rapidly and the oxidation reaction occurred. 0.5 mL of the reaction mixture was sampled at 20-min intervals. Each sample was diluted to 100 mL with deionized water and its absorbance at 290 nm was measured to quantify the amount of cinnamaldehyde.

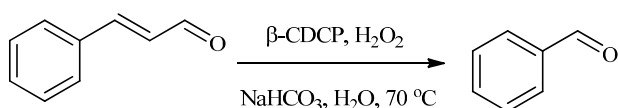
2.6. Computer modeling of the inclusion complex of cinnamaldehyde or benzaldehyde with β -CDCP

2.6.1. Thermodynamic properties of the inclusion complex in a vacuum

Molecular dynamic (MD) simulations were performed with Material Studio version 4.3 (Accelrys, Boston, USA). A COMPASS force field was employed in all MD simulations according to previous reports [25]. The structure of β -CD with cinnamaldehyde or benzaldehyde was first energy optimized, and then subjected to an inclusion molecule. The models were constructed at a fixed 1:1 molar ratio of cinnamaldehyde or benzaldehyde to β -CD in β -CDCP. The binding energy (BE) can be expressed as:

$$\text{BE} = E_{\text{C}} - E_{\text{G}} - E_{\text{H}} \quad (1)$$

where E_{C} , E_{G} , and E_{H} were the total energy of inclusion complex, guests, and host, respectively. β -CDCP was used as the host, and



Scheme 1. Oxidation of cinnamaldehyde to benzaldehyde catalyzed by β -CDCP.

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