Journal of Catalysis 327 (2015) 78–85

Contents lists available at ScienceDirect

Journal of Catalysis

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

Biochemical composite synthesized by stepwise crosslinking: An efficient platform for one-pot biomass conversion

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ARTICLE INFO

Article history:
Received 16 March 2015
Revised 18 April 2015
Accepted 20 April 2015

Keywords:
Biochemical composite
Yolk–shell nanostructure
Metallic catalysis
Enzymatic catalysis
Biomass conversion

ABSTRACT

This paper describes the development of a new bifunctional catalyst system that integrates enzyme and chemical material into a biochemical composite through a stepwise crosslinking approach. The as-prepared biochemical composite not only allows "one-pot" biomass conversion *via* sequential enzyme-catalyzed hydrolysis of biomass materials to glucose and metal-catalyzed hydrogenation of glucose to sorbitol, but also enables reusability of the catalyst. This design concept facilitates access to fuels and chemicals from the biomass-derived sorbitol and will attract more attention in the foreseeable future.

1. Introduction

The production of fuels and chemicals from plentiful and renewable biomass resources has drawn immense attention in recent years [1–5]. Sorbitol, a hexitol, is a valuable platform chemical that can be converted by straightforward methods into a variety of useful products [6]. Nowadays, almost all extant sorbitol production processes are usually based on the hydrogenation of glucose catalyzed by metallic catalysts [7–13]. In fact, glucose can be facilely obtained from biomass materials, primarily starch [14–16] and even cellulose, [17] through enzymatic hydrolysis bioprocesses. Apparently, a combined, one-pot hydrolysis–hydrogenation of biomass materials to sorbitol displays some advantages in its step-saving and low costs mainly linked to both the separation and the refining procedures [18–20]. Nevertheless, our previous studies revealed the one-pot process contains incompatible parameters. More specifically, enzymes are easily poisoned when contacting with metal catalysts, while metallic active sites would be covered by enzymes and the colloidal substances originated from hydrolysis of biomass materials, leading to a rapid deactivation for the subsequent glucose hydrogenation. Noting that encaging a functional material within another material can form a yolk–shell configuration that provides protecting effect on the individual core [21], very recently, we designed yolk–shell nanoarchitectures consisting of cores made of supported Ru encapsulated within porous silica shells [22,23]. By combining such materials with amyloglucosidase, one-pot hydrolysis–hydrogenation of dextrin has been successfully conducted to produce sorbitol where the porous silica shell separates the incompatible catalysts in different regions. Specifically, the enzymatic hydrolysis of dextrin to glucose occurs outside the yolk–shell nanoarchitectures owing to the blocking effect of the silica shells on the large enzyme molecules. Meanwhile, the permeation-selective porous silica shells offer a convenient path for the produced small glucose molecules crossing into the catalytically active cores for hydrogenation to sorbitol. While promising, the present process still uses free enzyme which decreases the economical attractiveness owing to the difficulty associated with the reusability of enzyme and the protein contamination of the final product. Therefore, immobilization of enzyme directly onto the outer surface of shell is needed to ensure the achievement of a real merging of such yolk–shell nanostructures and enzyme.

With advances in material science, a number of techniques have been developed for enzyme immobilization, such as support binding (physical binding, ionic binding, or covalent binding), entrapment, and crosslinking [24]. To enhance the operational stability and reusability of amyloglucosidases for bioprocessing,

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http://dx.doi.org/10.1016/j.jcat.2015.04.021
0021-9517/

they have been immobilized *via* various methods by far. Using polyethyleneimine-coated sepabeads as supports, Torres et al. successfully immobilized glucoamylase *via* ionic adsorption [25]. In comparison with ionic binding, covalent binding of enzyme to insoluble carriers is even stronger. In 2008, Kamal et al. reported the covalently immobilization of glucoamylase on polypropylene-grafted fibers by using carbodiimide as a coupling agent [26]. By using glutaraldehyde [27] or polyglutaraldehyde [28] as coupling agent, amyloglucosidase was attached to silanized magnetic nanoparticles or gelatin. Compared to other coupling agents, glutaraldehyde-based coupling reaction requires mild conditions. In those reports, immobilized amyloglucosidases were found to be more beneficial relative to the corresponding free enzymes. Despite the well-known advantages for enzyme immobilization, the immobilization of amyloglucosidase has not been performed frequently in industrial because the macromolecular enzyme loading is still a tough issue. Crosslinking technique has proved to be a promising approach for carrier-free immobilization of enzyme, which permits multipoint attachment through intermolecular crosslinking between enzyme molecules [29]. Based on this technique, Talekar et al. recently developed a combi-CLEAs strategy to prepare carrier-free co-immobilization of macromolecular enzymes, glucoamylase, and pullulanase [30]. In our research, we sought to address these concerns by *both* covalently attaching of yolk–shell nanostructures onto amyloglucosidase *and* ensuring an insoluble and robust biochemical catalyst.

Herein, we design a recyclable bifunctional biochemical composite. The synthesis of such composite is achieved through a stepwise crosslinking method that involves the covalent attachment of yolk–shell structured chemical catalyst onto amyloglucoamylase with glutaraldehyde and the subsequent coupling of the composite in the presence of modified dextran. The biochemical composite enables the efficient synthesis of sorbitol in one pot from dextrin, cellobiose, and even cellulose. More importantly, the biochemical composite could be used repetitively many times, showing a good potential in industrial applications.

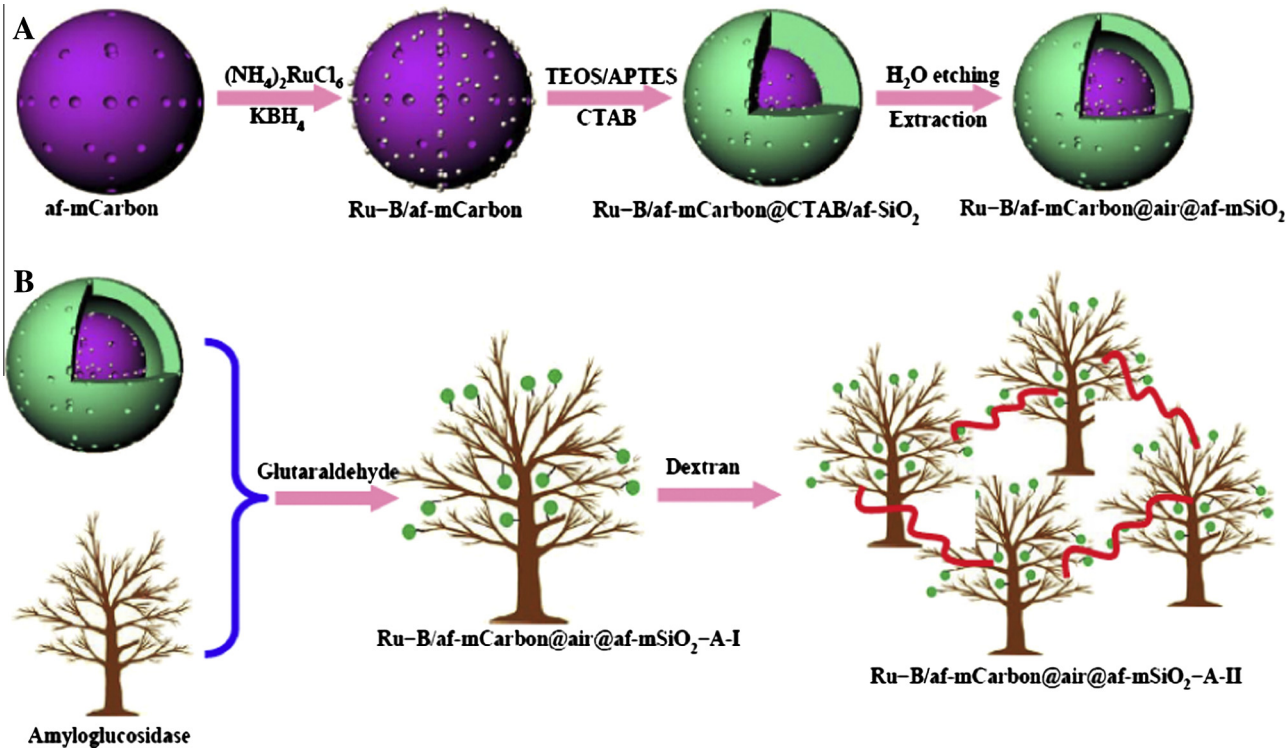
2. Experimental section

2.1. Catalyst preparation

The synthesis of biochemical composite involves the fabrication of yolk–shell structured chemical catalyst (Scheme 1A) and the integrating of the above material and enzyme (Scheme 1B). Firstly, uniform dispersing of Ru–B amorphous alloys within the porous channels of amino-functionalized mesoporous carbon nanospheres (af-mCarbon) was achieved by ultrasound-assisted incipient wetness infiltration of $(NH_4)_2RuCl_6$ onto af-mCarbon, followed by reduction with borohydride (Ru–B/af-mCarbon) [31]. Afterward, the Ru–B/af-mCarbon was coated by co-condensation of tetraethoxysilane (TEOS) and N-(amino-ethyl)-amino-propyl trimethoxy silane (APTES) in the presence of cetyltrimethylammonium bromide (CTAB), generating a core–shell structured Ru–B/af-mCarbon@CTAB/af-SiO_2, where CTAB/af-SiO_2 refers to a mesostructured CTAB/silica composite coated on the surface of the Ru–B/af-mCarbon core. Finally, the as-synthesized core–shell structured Ru–B/af-mCarbon@CTAB/af-SiO_2 was etched with hot water to achieve a yolk–shell structured configuration (Ru–B/af-mCarbon@air@af-mSiO_2). The integrating of the yolk–shell structured Ru–B/af-mCarbon@air@af-mSiO_2 and enzyme was conducted through a stepwise crosslinking method, including covalent attachment of chemical catalyst onto enzyme through a glutaraldehyde-based crosslinking technique (Ru–B/af-mCarbon@air@af-mSiO_2–A-I) and coupling of the obtained crosslinked composite with modified dextran (Ru–B/af-mCarbon@air@af-mSiO_2–A-II). More details about the catalyst preparation can be found in the Supporting Information.

2.2. Catalyst characterization

Fourier transform infrared (FTIR) spectra were obtained using a Thermo Nicolet Magna 550 spectrometer. The bulk composition



Scheme 1. Illustration of the synthesis process of (A) yolk–shell structured Ru–B/af-mCarbon@air@af-mSiO_2 and (B) biochemical composite through stepwise cross-linking technique.