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Review

Chemocatalytic hydrolysis of cellulose into glucose over solid acid catalysts

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ABSTRACT

With the progressive increase in global energy demands and the continuous depletion of worldwide fossil resources, renewable lignocellulosic biomass has attracted more and more attention. As the most abundant component of lignocellulosic biomass, cellulose, which is a linear polymer formed by the repeating connection of glucose units through β-1,4-glycosidic linkages, is considered to be an inexhaustible raw material for the sustainable production of chemicals and fuels. For the effective utilization of cellulose, the primary and essential step is the hydrolysis of cellulose into glucose. Although homogeneous acids and cellulases are the most common catalysts for the hydrolysis of cellulose into glucose, they possess a series of problems such as reactor corrosion, waste treatment and poor recyclability and high cost, low efficiency and long reaction time, respectively. In order to overcome the above-mentioned drawbacks, solid acid catalysts have been increasingly employed for the hydrolysis of cellulose into glucose in recent years. In this review, the state-of-the-art studies on the hydrolysis of cellulose into glucose over various types of solid acid catalysts such as acid resins, metal oxides, H-form zeolites, heteropoly acids, functionalized silicas, supported metals, immobilized ionic liquids, carbonaceous acids and magnetic acids are systematically summarized. Meanwhile, reaction medias, auxiliary methods and neoteric strategies for the hydrolysis of cellulose into glucose are intensively discussed. Furthermore, some potential research trends in the future are also prospected to provide some valuable ideas for the hydrolysis of cellulose into glucose in a more green, simple, efficient and inexpensive way.

Contents

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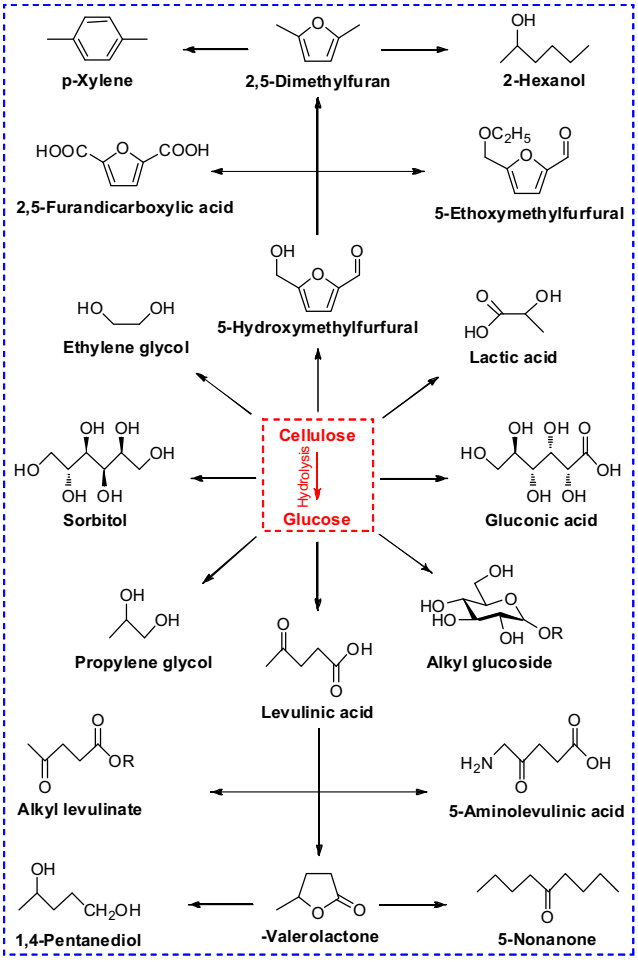
1. Introduction

Among various renewable resources, lignocellulosic biomass, possessing a range of excellent properties such as widespread, abundant, diverse and inexpensive, is regarded as a promising and appealing alternative to nonrenewable fossil resources [1–8]. As estimated, nature produces 200 billion metric tons of lignocellulosic biomass with an energy content of 3×10^{18} kJ year^{-1} by photosynthesis, which is around 10 times the present and annual energy consumption of the world [9–12]. Under the drive of a huge potential of lignocellulosic biomass, many countries in the world have launched the corresponding research and development plans such as America's "Energy Farm", Brazil's "Alcohol Program", India's "Renewable Energy Scenario" and Japan's "Sunshine Project" [13]. As is known to all, cellulose is the most abundant component of lignocellulosic biomass [14–20], its effective utilization is of great importance to reduce the excessive dependence on fossil resources, alleviate the energy crisis and decrease the environmental pollution. In recent years, the selective transformation of cellulose into a variety of high-value chemicals and high-quality fuels (Scheme 1) has been becoming one of the most interesting and attractive issues in the field of biorefinery [21–34]. However, it should be pointed out that the hydrolysis of cellulose into glucose is the starting point and entry point of biorefinery [35–39], which is crucial to the whole selective transformation chain.

In a long period of time, considerable attention has been concentrated on homogeneous acids and cellulases for the hydrolysis of cellulose into glucose. Sulfuric acid (H_2SO_4), nitric acid (HNO_3), perchloric acid ($HClO_4$), phosphoric acid (H_3PO_4), hydrochloric acid (HCl), hydrofluoric acid (HF) and formic acid (FA) are known as a typical type of homogeneous acids [40–48]. Although they exhibit reasonable prices and good catalytic activities, their practical applications are difficult due to a lot of problems including reactor corrosion, waste treatment and poor recyclability as well as severe reaction temperature [49–54]. In contrast to homogeneous acids, cellulases that can be derived from *Trichoderma reesei*, *Aspergillus niger*, *Aspergillus nidulan* and *Penicilinium funiculosum* are more selective and competitive to hydrolyze cellulose into glucose at lower reaction temperature [55–59]. However, enzymatic hydrolysis of cellulose is a slow process, which will spend a long time to achieve a satisfactory yield of glucose [60–62]. In addition, prior to enzymatic hydrolysis of cellulose into glucose, an energy- and cost-intensive pretreatment is needed to remove the recalcitrance to cellulases [63–65]. More unfortunately, cellulases are still very expensive in the present, making them unacceptable to pursue high hydrolysis rate by increasing the amount of cellulases [66–69]. From the viewpoint of green chemistry and industrialization, solid acid catalysts such as acid resins, metal oxides, H-form zeolites, heteropoly acids, functionalized silicas, supported metals, immobilized ionic liquids, carbonaceous acids and magnetic acids, which are separable, recoverable and reusable, should be the excellent choices for the hydrolysis of cellulose into glucose, because they have a tremendous potential to overcome the above-mentioned limitations [16]. In other words, solid acid catalysts can open up an opportunity to explore more efficient, economical, simpler and greener processes for the hydrolysis of cellulose into glucose [50]. More gratifyingly, more and more interest has been devoted to the hydrolysis of cellulose into glucose by using various types of solid acid catalysts. In 2009 and 2013, Rinaldi and Schüth [35] and Huang and Fu [60] have reviewed some available advancements on the hydrolysis of cellulose into glucose with solid acid catalysts, respectively. However, this research field is progressing very fast and many significant findings are continuously observed. Hence, a real-time and comprehensive review is also needed.

In this review, in addition to summarizing the latest applications and achievements of solid acid catalysts, much special emphasis



Scheme 1. Selective transformation of cellulose into various chemicals and fuels via glucose.