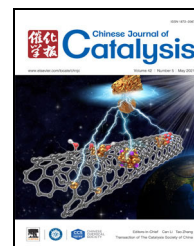


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Article

Production of bio-ethanol by consecutive hydrogenolysis of corn-stalk cellulose



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ABSTRACT

Current bio-ethanol production entails the enzymatic depolymerization of cellulose, but this process shows low efficiency and poor economy. In this work, we developed a consecutive aqueous hydrogenolysis process for the conversion of corn-stalk cellulose to produce a relatively high concentration of bio-ethanol (6.1 wt%) without humin formation. A high yield of cellulose (ca. 50 wt%) is extracted from corn stalk using a green solvent (80 wt% 1,4-butanediol) without destroying the structure of the lignin. The first hydrothermal hydrogenolysis step uses a Ni-WO_x/SiO₂ catalyst to convert the high cumulative concentration of cellulose (30 wt%) into a polyol mixture with a 56.5 C% yield of ethylene glycol (EG). The original polyol mixture is then subjected to subsequent selective aqueous-phase hydrogenolysis of the C–O bond to produce bioethanol (75% conversion, 84 C% selectivity) over the modified hydrothermally stable Cu catalysts. The added Ni component favors the good dispersion of Cu nanoparticles, and the incorporated Au³⁺ helps to stabilize the active Cu⁰-Cu⁺ species. This multi-functional catalytic process provides an economically competitive route for the production of cellulosic ethanol from raw lignocellulose.

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1. Introduction

Bio-ethanol is a promising green and renewable liquid fuel that is used as a gasoline additive. First generation bio-ethanol production involves the sequential hydrolysis and fermentation of grain. To avoid the use of agricultural crops to produce liquid energy sources, the sustainable biomass cellulose is considered to be a new, more promising resource for bio-ethanol production. The current technique for the production of ethanol from cellulose involves enzymatic hydrolysis of the cellulose to produce sugar and subsequent fermentation to produce bio-ethanol [1]. However, this bio-fermentation process shows low activity and low atom economy, i.e., 1 mol sugar produces 2

mol CO₂ and 2 mol ethanol [2,3]. Therefore, the development of advanced catalytic approaches for the conversion of high concentrations of cellulose is highly desired.

Compared to enzymatic catalysis, the transformation of cellulose into bio-ethanol via heterogeneous catalysis is more attractive due to its high efficiency. Zhang and co-workers [4,5] introduced a pioneering two-step process for the conversion of cellulose into bio-ethanol that involves the formation of methyl glycolate (MG) over a WO_x catalyst using 1 MPa O₂ at 240 °C, followed by the hydrogenation of MG to bio-ethanol over Pt-Cu/SiO₂ at 180 °C and 3 MPa H₂. To avoid the risks associated with O₂, the same group developed a one-pot process for the hydrogenation of cellulose into bio-ethanol (43.2 C%) over a

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