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Heterobimetallic catalysis for lignocellulose to ethylene glycol on nickel-tungsten catalysts: Influenced by hydroxy groups

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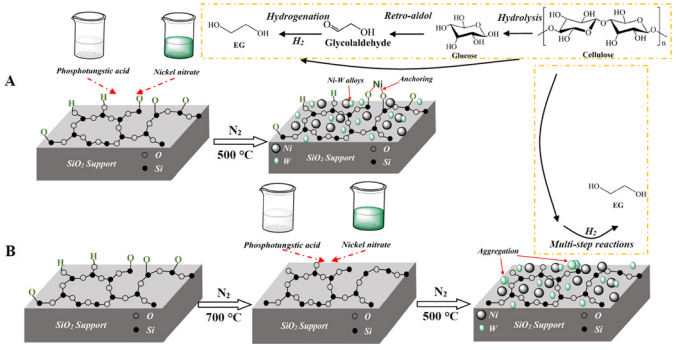
GRAPHICAL ABSTRACT

The formation of Ni_xW_y alloys on the surface of Ni-W/SiO_2 catalyst promoted the catalytic efficiency by catalyzing the unsaturated intermediates to polyols. This process decreased the accumulation of unsaturated intermediates and reduced the probability of the unsaturated intermediates conversion to organic acid.



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ABSTRACT

The superficial chemical environment of the catalyst supports played an important role in heterometallic catalysts preparation. The functions of hydroxy groups on the surface of SiO_2 nanosphere was investigated in catalyst preparing and cellulosic biomass conversion to ethylene glycol (EG). The results demonstrated that 15% Ni-20%W/SiO_2-OH catalyst was favorable for EG production, with the highest yield of 63.1 and 42.1% from microcrystalline cellulose and hardwood pulp, respectively. The characterization and activity tests suggested that the existence of hydroxy groups could promote the formation of more Ni-W alloys (e.g. NiW, Ni_4W) under the same preparing condition, which supplemented and enhanced the incorporation of intrinsic nickel and tungsten catalytic activity, especially for enhancement of retro-aldol condensation reaction. Moreover, the metallic Ni^0 was generated in higher amount when supported on hydroxy-rich SiO_2, boosting hydrogenation of the unsaturated intermediates. Finally, the reusability investigation of the catalyst implied that embedded Ni and W in alloys could inhibit leaching of metals in pressurized hot water.

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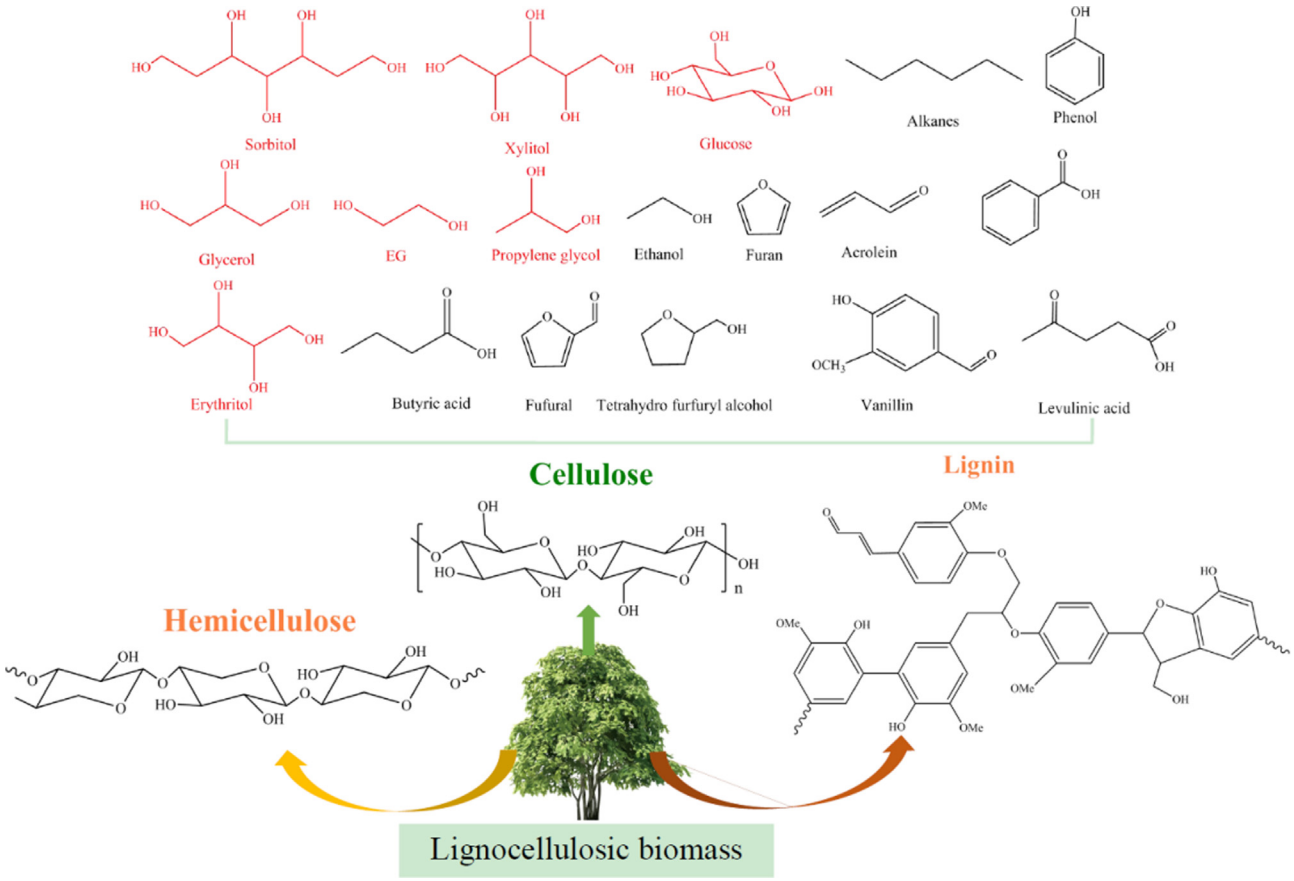

Scheme 1. The conversion of lignocellulosic biomass to platform chemicals.

1. Introduction

Although flammable ice and natural gas has been studied and developed recently, some great challenges, such as exploitation, storage and transportation, hinders their effective utilization. Lignocellulosic biomass has been regarded as an extraordinarily large amount of renewable bio-resource available in application of producing green chemicals for human sustainability [1]. The main composition of lignocellulosic feedstocks is cellulose, hemicellulose and lignin. However, the great challenges are the obstacles associated with effective utilization of lignocellulosic materials because of its recalcitrance. Hence, the lignocellulosic biomass requires physical, chemical or the coupling pretreatment to increase accessibility to catalytic methods in order to achieve acceptable oil alternative chemicals [2,3], such as polyols, furans, alkanes, sugars, etc. (Scheme 1). Cellulose is one of the ingredients of lignocellulosic biomass, composed of linear β-1,4-linked D-glucopyranose chains tightly packed, which are highly recalcitrant to be hydrolyzed via the ordinary strategies [4]. Simultaneously, cellulose is the main renewable material for producing bio-based low carbon chemicals, including $C_{2,3}$ polyols [5], levulinic acid (LA) [6], ethanol, methyl glycolate [7], lactic acid [8] and N-heterocyclic compounds [9]. Hemicellulose has been proposed as a possible feedstock for the production of ethanol [10] and C_5 sugars including xylose, arabinose [11]. Among these bio-based renewable alternatives of fossilized derivatives, EG is one of the most highlighted target molecule. It could be used as a precursor and coating agent in the plastics and food industries such as for polyester fibers and polyethylene terephthalate (PET). Moreover, EG also could serve as an antifreeze or coolant liquid in vehicles. The shortage of petrochemical resources provides the opportunities for us to develop strategies of the bio-EG production. It is reported that the Coca Cola Company has already employed 30% bio-EG for its Plant Bottle packaging [12].

However, the great challenge of cellulose or lignocellulose conversion to EG through catalytic hydrogenolysis is how to establish the high efficient catalytic system. In the past decades, many reports had been published, primarily by Zhang, Sels and their coworkers, who described several efficient catalytic systems. A hot report published in 2008 was about the direct conversion of cellulose to EG in one pot using Ni-W_2C/AC catalyst with 61% yield of EG [13]. Afterwards, Zhang developed the nickel-tungsten catalysts for this process. It was almost ascertained that the tungsten and nickel based species were the more active metallic sites, especially for the formation of EG. EG yield could reach up to 76.1% via Ni-W/SBA-15 catalysts at 245 °C in 6.0 MPa H_2 for 30 min [14]. Successively, some other bi-functional catalyst agents also had recently been further studied, such as Ru/C + W_2C mixed catalysts [15], Ni-Sn [16,17], WO_3-ZrO_2 [18] and CuCr catalysts [18], etc. It has been established that the one-pot conversion of cellulose to low carbon ($C_{2,3}$) polyols proceeding through hydrolysis, retro-aldol condensation, hydrogenation and isomerization. Hence, the ideal catalyst might have one or more active sites to match the catalytic assignment in the conversion. Eissa et al. incorporated three different metals into the mesoporous materials (Al-W-Ni/TUD-1), exhibiting the high cellulose conversion and the EG yield was 76% [19]. Except these, there is an another fundamental factor which will have an obvious influence on catalytic efficiency. Understanding the properties of the supporters surface is the fundamental research, such as the structures, functional groups, energy distribution of the supports including SiO_2, SBA-15, AC and CNTs, etc. Based on the properties of supports surface, we can design the strategy to modify the surface and study the interaction between supports and metals in specific catalytic system [20,21]. Meanwhile, hydroxy groups were very important functional groups existed on surface of many popular supports, which are closely related