Self-reducing bifunctional Ni-W/SBA-15 catalyst for cellulose hydrogenolysis to low carbon polyols

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A B S T R A C T

A series of self-reducing bifunctional Ni-W/SBA-15 catalysts were synthesized using biomass-based carbon source as the reducing agent without conventional further reduction step. The self-reducing catalysts were performed on the hydrogenolysis of cellulose to low carbon polyols. The effects of calcination temperature and metallic loading contents for cellulose hydrogenolysis reaction were investigated detailedly. The optimal calcination temperature was found to be 673 K by TG analysis. The active metal nanoparticles with a better dispersion were observed using SEM and element mapping technology. The yield of low carbon polyols using the catalyst with the receipt of 10%Ni-15%W/SBA-15-673 K can reach as high as 68.14%, of which the ethylene glycol (EG) accounts for 61.04%.

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1. Introduction

Nowadays, the impact of anthropogenic CO_2 and other acidic waste gas emission from fossil energy is a major cause of environmental degradation. Biomass, as an abundant and renewable material, appears to be an alternative and attractive feedstock of fossil energy for chemical production. The controllable refining process of biomass has been the research hot spot of worldwide scale because it can be applied to biochemicals and biofuels. Based on the molecular carbon content, the biomass refining products can be divided into the following categories: C_1 (methane, methanol, etc.), C_2 (ethanol, acetic acid, ethylene glycol, etc.), C_3 (lactic acid, acrylic acid, propylene glycol, etc.), C_4 (succinic acid, fumaric acid, butyl glycol, etc.), C_5 (itaconic acid, xylitol, etc.) and C_6 (citric acid, sorbitol, mannitol, etc.). In recent years, much attention has been paid to the lignocellulosic and nonfood biomass due to the abundant biomass in nature.

Yielding the high value-added chemicals effectively and selectively from cellulose is concerned with the direction utilization of

biomass resource, whereas its crystalline nature and strong intra-hydrogen bonds make cellulose hardly dissolve in water or other conventional solvents. That is why it has been the huge challenge to the degradation of cellulose [1]. At present, the degradation of cellulose generally requires chemical catalysis. For instance, one-pot transformation of cellulose to target products mainly relies on the chemical catalytic process including hydrolysis, hydrogenolysis or hydrogenation. Mineral acids (H_2SO_4, HCl, H_3PO_4, etc.) showed effective catalytic activity for hydrolysis of cellulose [2]. However, the great obstacles, such as equipment corrosion, waste water emission and separation of water-soluble acids from liquid phase were inevitable [3]. Solid acid catalysts [4], including heteropoly acid, high state transition metal salts ($PW_{12}O_{40}^{3-}$, etc.) and immobilized sulfonic acid catalysts ($AC-SO_3H$, etc.), are prone to provide H^+ in hydrothermal condition, promoting catalysis of the cellulose hydrolysis into mono/oligo-saccharides. However, in the hot and acidic aqueous solution, glucose and other saccharides, as the cellulose hydrolysis products, tend to be carbonized after dehydration, which leads to more by-products [3]. Comparatively, bifunctional solid catalysts contain metals (Ni, Ru, W, Pt and other transition or noble metals) loaded on acidic supports with a better hydrothermal stability, such as Al_2O_3 [5], ZSM-5 [6], activated carbon (AC) [7,8], CMK-3 [9] and SBA-15 [10,11]. Support types have drawn a great deal of interest because of its recyclable and environmentally benign advantages. In the actual process of preparation, the ratios
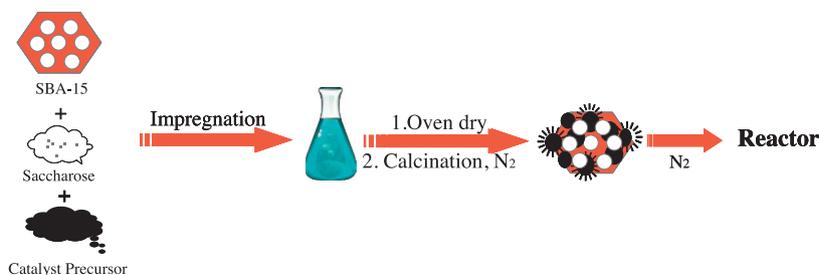
Fig. 1. The process of preparation for self-reducing bifunctional catalysts.

of active metals and the carrier acid have been extensively investigated to improve the activity of solid bifunctional or multifunctional catalysts. According to the literatures, metal catalysts were reduced usually before reaction under the hydrogen atmosphere [12–14]. Moreover, additional reduction devices are required for the reduction process of the catalysts. And the catalysts may be oxidized again in a long period of operation when transferring from reduction device to reactor. This would affect the performance of the whole cellulose conversion.

To solve the problem, some researchers reported a one-step method using solid-liquid grinding/templating route with some biomacromolecule, such as soybean oil to synthesize mesostructure carbon composites or self-reducing magnetic catalysts for organic synthesis [15,16]. However, there was no report on the application of self-reducing catalyst to cellulose hydrogenolysis process. Moreover, one of the most obvious disadvantages of this method is the production of large quantity of mixed catalysts precursors caused by grinding/templating, which would lead to producing more large size particles of active components after calcinations and this would prevent the efficient contact between the catalysts and reactants. Therefore, the development of a simple and effective method for the self-reducing catalysts with a better dispersion is necessary and challenging.

To investigate the effect of the reducing gas (produced in the process of catalysts calcination at high temperature) on the reduction of active metals (such as Ni), we designed an experiment to adopt an incipient-wetness impregnation method and the new bio-carbon source in the process of preparing catalysts. This design aimed at skipping the reduction step in preparing the catalyst before the reaction followed. In this paper, we examined the calcination temperature, the content and ratio of active metals on the influence of cellulose conversion. The reaction results showed that under the same reaction conditions, the optimum catalysts calcination temperature is 673 K and the yield of ethylene glycol (EG) was 61.04% with the content of nickel and tungsten of 10% and 15%, respectively.

2. Experimental

2.1. Materials

Cellulose (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. microcrystalline), SBA-15 (Nanjing XFNANO Materials Tech Co., Ltd., Nanjing, China.), Phosphotungstic acid ($H_3PO_{40}W_{12} \cdot xH_2O$, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.), Nickel nitrate hydrate ($Ni(NO_3)_2 \cdot 6H_2O$, Energy Chemical Co., Ltd, Shanghai, China.), and Sucrose (Shanghai Kerry Food Industry Co., Ltd., China.).

2.2. Preparation of catalysts

Self-reducing bifunctional catalysts Ni-W/SBA-15 were prepared as shown in Fig. 1. All the catalysts were prepared by the incipient-wetness impregnation method. Before the beginning of the preparing process, the bibulous rate of SBA-15 was investigated. SBA-15 was firstly impregnated with an aqueous solution containing phosphotungstic acid and nickel nitrate hydrate. The impregnation volume of metal solution was calculated using the measured incipient wetness of SBA-15. Subsequently the 1.0 g, 2.0 g, 3.0 g, 4.0 g and 5.0 g sucrose were added into the above-mentioned mixture, respectively. And then the impregnated catalysts were oven dried at 363 K for 10 h and then calcinated at 573–1073 K in pipe calciner for 5 h at the atmosphere of nitrogen. And the nitrogen was conected with pipe calciner continuously. After calcination, the catalysts were nitrogen cooled to below 313 K in pipe calciner before transferring to the reactor under the protection of nitrogen.

2.3. Catalysts characterization

The catalysts crystal structure and species determination were carried out by PW3040/60 X'pert Pro type ray diffractometer (PAN-alytical B.V., Netherlands), and Cu $K\alpha$ radiation, rated output power was 3 kW, and the scanning speed was 5°/min.

Scanning electron microscope (SEM) characterization was conducted by Japan's HITACHI S 4800 scanning electron microscope (HITACHI, Japan) with the accelerating voltage of 15 kV. Element distribution characterization (Element Mapping) was carried out by EMAX 7593 type spectrometer (Horiba, Japan).

Catalyst thermogravimetric analysis (Thermogravimetry, TG) was done by STA 449 of F3 Jupiter synchronization comprehensive thermal analyzer (Germany NETZSCH, Germany). The heating rate was set at 10 K/min from room temperature to 1173 K under the mixed flow rate of air (20 mL/min) and the nitrogen (10 mL/min).

The surface composition of Ni-W/SBA-15 was analyzed by X-ray photoelectron spectroscopy (XPS) on a K-alpha spectrometer (Thermo Fisher Scientific, USA) with an Al $K\alpha$ X-ray source (1486.6 eV, 15 kV, 150 W). The C 1 s peak at 285 eV was used as the reference for all binding energies. The photo-peak area was determined after the subtraction of the linear spectral background. The spectral simulations were based on a Gaussian profile.

2.4. Performance of the catalysts

The series of cellulose hydrogenolysis reactions were carried out in a 100 mL stainless steel autoclave (KF, Electronic equipment Co., Ltd, Dalian, China.). Firstly, 55 mL deionized water, 0.50 g cellulose and 0.20 g catalyst were charged into the autoclave. After the replacement of the air by hydrogen, the reactor was filled with hydrogen continuously until the hydrogen pressure reached 5.0 MPa (at room temperature). Timing starts when reactor's preset reaction temperature was reached under stirring. After the reactions were achieved, the reactor was cooled to room temperature with cold running water. The reaction mixtures were transferred to a container after the pressure was released. Keep the liquid part and the solid residues were filtered off.