Fuel 215 (2018) 406–416

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Metal particles supported on SiO_2-OH nanosphere: New insight into interactions with metals for cellulose conversion to ethylene glycol

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ARTICLE INFO

Keywords:
Cellulose
Hydrogenolysis
Ethylene glycol
Interaction
Metallic catalysts

ABSTRACT

The catalytic transformation of cellulose to polyols is one of the significant strategies to overcome the shortage of fossil fuels. Here we report a simple but effective preparation method for Ni-W/SiO_2 catalysts by introduction of chelating agents (ammonium hydroxide and ethanediamine) coupled with organic reducing agent (ethylene glycol). The ethylene glycol (EG) yield from microcrystalline cellulose could reach up to 63.3% at 240 °C, 5.0 MPa H_2 for 2.0 h over 15%Ni-20%W/SiO_2-EEG catalyst. Moreover, some key parameters of process conditions including calcining temperature, reaction temperature and time, H_2 pressure and the recycling use of catalysts were investigated. Both theoretical and experimental studies suggested that 15%Ni-20%W/SiO_2-EEG catalyst showed the best activity and stability for cascading steps for EG formation at this reaction condition. By the detailed analysis of Ni-W/SiO_2 catalysts after calcination via FT-IR, XRD, XPS, thermogravimetry (TG), TEM and element mapping, it could be concluded that on the surface of 15%Ni-20%W/SiO_2-EEG catalyst, the particles showed less agglomeration and more homogeneous on the surface of SiO_2. Some Ni_xW_y alloys (NiW, Ni_2W_4C) were also formed. Furthermore, it was found that the introduction of ethanediamine could promote the actual loading of nickel and tungsten species slightly according to the analysis of ICP-OES test.

1. Introduction

Nowadays, the direct catalytic transformation of cellulose, which is one of the main components of lignocellulosic biomass, to building-block bio-based chemicals received considerable attention due to the sustainability of this biorefinery process. Cellulose is the predominant cell wall polysaccharide, consisting of linear chains of 1,4-linked β-D-glucopyranosyl and it is the most abundant and non-edible lignocellulosic biomass on earth [1]. It is estimated roughly that about 1.7 trillion tons of photosynthesis production emerged as biomass, approximately 35–50% of which is cellulose [2]. Therefore, exploiting a new strategy or developing the existing methods to disrupt the recalcitrant structure of cellulose and then producing some important platform chemicals is necessary for our sustainable development. In recent years, one-pot conversion of cellulose to low carbon polyols ($C_{2,3}$) including ethylene glycol (EG), propylene glycol (PG) and glycol (Gly), and other important industrial intermediates such as methyl glycolate, furan, levulinic acid, ethanol and lactic acid, was developed as a hot field in biomass utilization [3,4,5–7].

The recalcitrance of cellulose, however, appears as the great challenge for oriented degradation under mild and environment-friendly conditions. As reported, the mineral acids like H_2SO_4, HCl and some organic acids such as carboxylic acids and *p*-toluenesulfonic acid showed good performance in hydrolysis of cellulose [8]. Nevertheless, these types of acid catalysts suffer from environmental issues. However, the recycling use of these acids is also a great challenge to match the green chemistry process. Meanwhile, the emerging enzymatic hydrolysis is still a high-cost and low efficiency method [3]. From this view, in contrast, developing a chemical catalytic process provides opportunities for hydrogenolysis of cellulose to chemicals including low carbon polyols with high efficiency and economical advantages. The study of bi-functional or multifunctional supported metallic catalysts is of great importance for this direction [9]. Recently, some researchers exploited the efficient metallic catalysts such as the series of nickel, tungsten and

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https://doi.org/10.1016/j.fuel.2017.11.086
Received 7 September 2017; Received in revised form 21 November 2017; Accepted 22 November 2017

other noble or transition metals based catalysts aiming at cleavage of glycosidic and C—C/C—O bonds in cellulose molecules. Fukuoka, Liu and coworkers developed the one-pot catalytic process for the selective conversion of cellulose into hexitols via Ru nano-catalyst in an aqueous solution [10–12]. Moreover, the employment of solid catalysts and using the water as the reaction medium dumb down the difficulty of separation of products and catalysts. Furthermore, Zhang, Wang, Palkovits, Bronstein and their groups found that the W [13], Ni [14,15] and Ru [16,20] sites supported on active carbon or modified SiO_2 showed the high selectivity for the formation of polyols from cellulose or pretreated lignocellulose. Because of its efficiency and low price, the nickel promoted catalysts have attracted extensive attention for a wide range of applications in cellulose conversion to $C_{2,3}$ polyols. The researchers have fabricated numerous structures of the catalysts depending on the desired surface, such as alloy type, core-shell type, porous structure or hollow spheres [17]. Due to their synthesis conditions and special architectures, the size, shape and stability of the active particles could be controlled. When the cellulose was introduced as the feedstock, the EG yield was selectively high (76.1%) via the catalysts of Ni-W/SBA-15 [13]. However, this catalytic result revealed that 72.6% yield of $C_{2,3}$ polyols showed the significant difference with the identical catalytic sites, such as nickel-tungsten catalysts [18,19,21], which demonstrated that many factors including interaction between metals, supports and the functional groups would affect the distribution of products obviously in cellulose conversion. In terms of particle dispersion, Yan, *et al.* discussed the rational control of the size, shape, composition and surface properties of nano-scale metal-catalysts for biomass conversion [22]. Generally, particles at nano- and sub-nanometers are more disordered, than in the bulk, increasing their surface activity because the high dispersion of particle promotes the mass transfer in this heterogeneous catalytic system. The cascade reactions in this process involving hydrolysis, retro-aldol condensation, isomerization and hydrogenation required multifunctional catalysts. The superficial micro-environment and the existing types of the metallic sites on the supports also should be known after a systematic investigation.

In our previous studies, a series of highly efficient catalysts including nickel-stannum catalysts [23], nickel-tungsten catalysts [4,24] were developed for the formation of EG from cellulose. According to the characterization of these catalysts and the catalytic results, we found that some strong interaction of metals happened after the calcining process, which seemingly had an influence on regulating the distribution of polyols. However, some details should be studied further. Inspired above, this work mainly focused on regulating the yield of low carbon polyols especially for the formation of EG by investigating the metallic interaction between nickel and tungsten on the surface of SiO_2-OH nanosphere, which has not been reported anywhere yet. Specifically, the Ni-W/SiO_2 catalysts were prepared by incipient-wetness impregnation method. In order to improve the loading capacity of SiO_2 nanosphere and suppress the formation of metal salts (such as Ni_2SO_3), we donated some chelating agents (ammonium hydroxide and ethanediamine) to convert the Ni^{2+} to the nickel clathrate in solution which could be decomposed easily. And then, the catalysts were reduced by reducing gas generating from EG in the process of calcination. Finally, the catalytic performance was evaluated by catalytic conversion of cellulose to polyols in aqueous solution.

2. Experimental

2.1. Catalyst preparation

The SiO_2-OH nanosphere supported nickel and tungsten (denoted as Ni-W/SiO_2) catalysts were prepared by the incipient wetness impregnation of 2.0 g SiO_2-OH nanosphere (Nanjing XFNANO Materials Tech., 300–430 m^2/g) with precursors solutions of $Ni(NO_3)_2{\cdot}6H_2O$ (AR, Energy Chemical) and $H_3PO_{40}W_{12}{\cdot}xH_2O$ (AR, Sinopharm Chemical Reagent). Notably, the concentration of $Ni(NO_3)_2{\cdot}6H_2O$ and $H_3PO_{40}W_{12}{\cdot}xH_2O$ solutions were calculated based on the mass of 2.0 g SiO_2. In this experiment, 1.50 g $Ni(NO_3)_2{\cdot}6H_2O$ and 0.52 g $H_3PO_{40}W_{12}{\cdot}xH_2O$ were added into 7.0 mL deionized water and then continued by impregnation process. But additionally and crucially, in order to change the nickel salts to the species which was easier to be decomposed and reduced successively, 2.0 mL ammonium hydroxide (AR, Longshan Chemical Co., Ltd.), 2.0 mL ethylenediamine (Zhanyun Chemical Co., Ltd.) and 2.0 mL ethylene glycol (Kelong Chemical Co., Ltd.) were introduced into the catalyst precursors solution with intensive agitation. To be noted, all the chelating agents above were added before the phosphotungstic acid was introduced into the solution. The impregnated samples were dried at 90 °C for 12 h. Finally, the samples were calcined at 500 °C for 5 h in a stable nitrogen flow. The catalyst samples were transferred into reactor under the protection of nitrogen.

2.2. Catalytic reaction and evaluation

All the catalytic experiments about cellulose conversion were carried out in a batch reactor (Yanzheng Equipment, 100 mL stainless steel autoclave). The typical reaction conditions were as follows: 0.50 g microcrystalline cellulose (Aladdin Bio-chem Tech), 0.20 g catalysts, 50.0 mL deionized water, initial hydrogen pressure of 5.0 MPa, reaction temperature was 240 °C and the stirring rate of 600 rpm for 2 h. After reaction, the liquid mixture was centrifuged to be separated from the solid residuum. The target products were analyzed by a high performance liquid chromatography (HPLC, Waters, USA) with a refraction index detector (RID 2414, Waters, USA) equipped a Welch X'mate-Ca (7.8 × 300 mm, 5 µm) column at 80 °C. Samples (injected 10 µL) were filtered through 0.45 µm millipore filter before HPLC analysis. Deionized water flow at the rate of 0.5 mL/min was used as the mobile phase. The cellulose conversion and the yield of production were calculated based on the mass of feedstock (M_0) as the following equations [15,18]:

$$\textit{Cellulose conversion}/\% = \frac{M_0 - M_1}{M_0} \times 100 \tag{1}$$

$$\textit{Yield of products}/\% = \frac{m_1}{M_0} \times 100 \tag{2}$$

where M_0 (g), M_1 (g) *and* m_1 (g) represent the mass of feedstock, residual cellulose after reaction and products respectively.

2.3. Catalysts characterization

FT-IR spectra experiments were tested with Nicolet iS 10 FT-IR instrument (KBr disc; Thermofisher, MA) over the range of 400–3000 cm^{-1} wave number. X-ray diffraction (XRD) patterns were recorded in the 2θ on a Ultima IV X-ray (Japan) diffractometer using a Cu Kα1 X-ray radiation operating at 40 kV and 100 mA. The 2θ angle was scanned in the range of 0–85° at the rate of 4°/min. 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 °C/min from room temperature to 900 °C under the mixed flow rate of air (20 mL/min) and the nitrogen (10 mL/min). The high-resolution transmission electron microscopy (HRTEM) experiments were conducted on a JEOL JEM-2100F microscope equipped with HAADF (high angle annular dark field) and Oxford detectors and STEM (Scanning transmission electron microscopy) and energy dispersive X-ray (EDX) spectra under 200 keV. The surface composition of Ni-W/SiO_2 was analyzed by X-ray photoelectron spectroscopy (XPS) on a *Kα* spectrometer (Thermo Fisher Scientific, USA) with an Al *Kα* X-ray source (1486.6 eV, 15 kV, 150 W). The survey spectra as recorded with the pass energy of 160 eV and the high-resolution spectra were collected with the pass energy of 40 eV. The binding energies were calibrated