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The hydrogenation/dehydrogenation activity of supported Ni catalysts and their effect on hexitols selectivity in hydrolytic hydrogenation of cellulose

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ABSTRACT

A series of Ni catalysts were prepared with various supports (ZSM-5, Al_2O_3, SiO_2, bentonite, TiO_2, and kieselguhr) and their catalytic properties were investigated for the hydrogenation of cellobiose and glucose, the reaction intermediates of cellulose hydrolysis in hot-compressed water, in order to elucidate the key factors to control the hexitols selectivity in the hydrolytic hydrogenation of cellulose. For the hydrogenation of cellobiose, hexitols were produced with a selectivity above 82% over Ni/ZSM-5, but the other checked Ni catalysts produced large amount of glycerol, ethylene glycol, and propanediol, and the product distribution strikingly depended on the catalysts used. On the basis of kinetic experiments, it was the hydrogenation/dehydrogenation ability of Ni catalyst that played a critical role in controlling hexitols selectivity. High hydrogenation and inferior dehydrogenation activity of Ni catalysts were essential for obtaining high yield of hexitols in the hydrolytic hydrogenation of cellulose. The synergistic effect of Ni active species and acid–base sites was proposed to accelerate the dehydrogenation of sorbitol and thus reducing the yield of hexitols.

1. Introduction

Cellulose is one of the most abundant forms of biomass on the earth, and the transformation of cellulose to fuels and chemicals has triggered more and more intense worldwide research interest. The efficient conversion of cellulose into target products through various catalytic processes has been regarded as one viable way to reduce the CO_2 emission and alleviate the energy crisis [1]. Chemical processes such as hydrolysis, gasification, and pyrolysis have been investigated for converting cellulosic biomass into chemicals. Specifically, one-pot catalytic conversion of cellulose into chemicals of polyols, ethylene glycol, and alkyl glycosides was developed, which is considered to be one of the most efficient methods [2–4]. So far, the hydrolytic hydrogenation of cellulose into polyols via one-pot method in hot-compressed water is a promising approach for its greenness and energy efficiency compared to other primary conversion processes. Fukuoka et al. firstly investigated the conversion of cellulose into sugar alcohols over supported noble metal catalysts and about 31% yield of hexitols (sorbitol and mannitol) was obtained by using Pt/Al_2O_3 catalyst within 24 h at 190 °C [5]. Liu et al. demonstrated that about 30% yield of sorbitol was obtained at 85.5% conversion of cellulose on supported Ru clusters within 30 min at 245 °C [6]. Various subsequent studies showed that Ru catalysts were highly efficient hydrogenation catalysts on cellulose conversion [6–10]. For example, Palkovits et al. demonstrated the introduction of dilute mineral acids could effectively promote the catalytic performance of supported Pt, Pd, and Ru catalysts on cellulose conversion, and their further research showed that the yield of sugar alcohols increased with combining heteropoly acids and Ru/C [9,11]. Sels et al. presented the combination of Ru-loaded zeolites and trace amounts of mineral acid could produce >90% yield of hexitols with complete cellulose conversion at mild conditions [8,12,13]. Wang et al. demonstrated the abundant acidic groups and lager Ru particles on Ru/CNTs could favor high yield of hexitols [7,14]. In our previous study, isosorbide could be obtained with a 50% yield from hydrogenation of microcrystalline cellulose over Ru/C catalyst with dilute hydrochloric acid at 215 °C and 6.0 MPa H_2 for 6 h [15]. Very recently, Sels et al. reported a more efficient way in isosorbide

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production by using $H_4SiW_{12}O_{40}$ and Ru/C, and 63% yield of isosorbide could be obtained from the fibrillar cellulose within 1 h [16].

All the above results are really promising; nevertheless, the selective hydrolytic hydrogenation of cellulose into polyols is still a big challenge. One significant disadvantage is the use of large amount of noble metal catalyst, making those approaches too expensive for the large-scale application in industry. Recently, attention is drawn to the non-noble metal catalysts, including Ni, Cu, and tungsten carbide catalysts because of the fast turnover rates, availability, and low cost. Zhang et al. studied the catalytic performance of Ni-promoted tungsten catalysts on cellulose hydrogenation; notably, ethylene glycol (EG) was obtained with 61% yield at 245 °C [17]. In their following research, tungsten carbide on mesoporous carbon (MC) and Ni-W/SBA-15 were demonstrated to be also effective for catalyzing cellulose and produced EG with the highest yield of 72.9% [18,19]. Conventional Ni-based catalysts have always been used as effective catalysts for aqueous-phase hydrogenolysis of sorbitol to produce glycerol, ethylene glycol, and propanediol. Unfortunately, supported Ni catalysts exhibited inferior performance in the transformation of cellulose into sorbitol. The attempts to increase activity and selectivity of Ni-based catalysts for the cellulose hydrogenation still encounter great difficulties. Therefore, the modified Ni-based catalysts are designed to promote the yield of sorbitol by suppressing the subsequent hydrogenolysis reaction. Sels et al. obtained 50% yield of sorbitol at 92% conversion of cellulose over the reshaped Ni particles on carbon nanofibers [20], their further study indicated that the metal active sites and the acidic functional group on Ni/CNFs should be properly balanced, and the 7.5 wt% Ni/CNFs with a relatively high amount of Ni surface atoms (26.9 mmol $g_{cat.}^{-1}$) and low density of Brønsted acid sites (0.02 $mmol_{H+}\,g^{-1}$) gave 76% yield of hexitols at a cellulose conversion of 93% [21]. Zhang et al. reported that nickel phosphides supported on activated carbon and SiO_2 were effective for conversion of cellulose to sorbitol, and about 48% yield of sorbitol was reached at complete conversion [22]. Moreover, they developed various Ni-based bimetallic catalysts using mesoporous carbon (MC) as support; more recently, nearly 60% yield of sorbitol was obtained over the Ir–Ni/MC catalyst [23]. In addition, they also developed a binary catalyst system composed of tungstic acid and Raney Ni which produced 65% of ethylene glycol [24]. 20% Ni/ZnO was reported to be one of the most effective catalysts among a series of the supported Ni catalysts, with it 70% yield of glycols (1,2-propanediol, ethylene glycol, 1,2-butanediol, and 1,2-hexanediol), which was obtained at complete cellulose conversion [25]. The above studies suggested that the support has a significant effect on the product selectivity in cellulose hydrogenation over the Ni based catalysts. However, the real role of Ni particles on the hydrolytic hydrogenation was still unclear as the whole process involved hydrolysis, hydrogenation, and hydrogenolysis steps was rarely studied. Specially, the relationship between the activity and the nature of hydrogenation catalysts in conversion of cellulose was still elusive.

For production of hexitols, a desired Ni catalyst should promote the hydrogenation of C=O bond in aldose or polysaccharide, but retard the further hydrogenolysis of hexitols or parallel reactions including aqueous phase reforming of polyols. We previously reported that Ni/ZSM-5 could efficiently catalyze cellulose into hexitol with about 91% selectivity at 48.6% conversion at 230 °C [26]. We demonstrated the Ni/ZSM-5 catalyst with petaloid-like nickel particles could not only favor the hydrogenation of the glucose formed, but also suppress the further hydrogenolysis of sorbitol, leading to a high yield of sorbitol. However, there is still little knowledge about the effect of the Ni catalysts on the conversion of cellulose to sorbitol. Therefore, it is essential to figure out the key factors that determine the production of hexitol. In this paper, the basic reaction steps in the hydrolytic hydrogenation of microcrystalline cellulose over Ni catalysts, including the hydrogenation of cellobiose and glucose, as well as the dehydrogenation of sorbitol, were discussed in order to figure out the correlation between the catalytic performance and the nature of the catalyst. The kinetic study demonstrated that the hydrogenation/dehydrogenation ability of Ni catalysts had significant influence on the catalytic activity and selectivity of Ni catalysts in converting cellulose into hexitols.

2. Experimental

2.1. Materials

Microcrystalline cellulose (relative crystallinity of about 74.6%, Alfa Aesar) was dried at 70 °C for 24 h before use. $Ni(NO_3)_2{\cdot}9H_2O$ (AR) was purchased from Sinopharm Chemical Reagent, SiO_2 (Sigma–Aldrich), TiO_2 (Sigma–Aldrich), γ-Al_2O_3, bentonite, and kieselguhr (Sinopharm Chemical Reagent) were used as received. ZSM-5 (NKF-5, H type, Si/Al = 25, 38, 50), HY, and USHY were purchased from the Catalyst Plant of Nankai University. Nano CuO was obtained from Aladdin.

2.2. Catalyst preparation

The supported Ni catalysts were prepared by a modified incipient impregnation method. In detail, a series of supports (Al_2O_3, SiO_2, ZSM-5, bentonite, kieselguhr, and TiO_2) were immersed in an aqueous $Ni(NO_3)_2$ solution with a certain concentration at room temperature. The mixture was treated under ultrasonic condition for 0.5 h and the solid suspension was formed. Then, the solid suspension was dried at 70 °C with stirring. During this process, the solvent was evaporated slowly until the solid suspension was dried to powder again. This process will take about 3 h; after that, the mixture was vacuum dried at 60 °C for 12 h, followed by calcinations under Ar atmosphere at 450 °C for 2 h with heating rate of 5 °C min^{-1}. Prior to reaction or characterization, all the catalysts were reduced under H_2 atmosphere for 2 h at appropriate temperatures with a heating rate of 5 °C min^{-1}.

2.3. Catalyst characterization

Powder X-ray diffraction of the samples was recorded on a Bruker D8 Advance X-ray diffractometer with a Cu Kα source (λ = 0.154 nm) in the 2θ range 10–80° with a scan speed of 10° min^{-1}.

H_2-temperature-programmed reduction (H_2-TPR), H_2-temperature-programmed desorption (H_2-TPD), and NH_3-temperature-programmed desorption (NH_3-TPD) were conducted on a Tianjin XQ TP-5080 chemisorption instrument with a thermal conductivity detector (TCD). As for H_2-TPR, 30 mg of fresh catalyst was loaded into a quartz reactor. Before H_2-TPR, the catalysts were heated at 150 °C for 30 min in nitrogen and then cooled to room temperature. The sample was reduced in a 10% H_2/N_2 flow with a heating rate of 10 K min^{-1}. The effluent gas was analyzed with a thermal conduction detector (TCD). As for the H_2-temperature-programmed desorption, 100 mg of each catalyst was loaded into a quartz reactor and then reduced with a H_2 flow at appropriate temperature. After reduction, the reactor was cooled down to room temperature and then the catalyst sample was maintained under H_2 flow for 30 min. Following the desorption step, the reactor was flushed with N_2 for 2 h to reach a stable background. At last, H_2-TPD was carried out with N_2 at a flow rate of 30 mL min^{-1} and a temperature ramp rate of 10 °C min^{-1}. The process of NH_3-TPD was same as that of H_2-TPD.