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Catalytic production of isosorbide from cellulose over mesoporous niobium phosphate-based heterogeneous catalysts via a sequential process

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ABSTRACT

The catalytic valorization of cellulose as feedstock for the large-scale production of liquid fuels and value-added chemicals is currently subject to extensive research. Isosorbide as an important intermediate for the synthesis of a wide range of pharmaceuticals, chemicals and polymers, its efficient production from natural cellulose is very important. Here we report a two-step sequential process where cellulose is firstly depolymerized with Ru/$NbOPO_4$-pH2 catalyst via hydrolysis and hydrogenation and then the resultant sorbitol and sorbitan are directly converted into isosorbide in the presence of solid acid catalyst. The influence of different solid catalysts is investigated in the direct dehydration of sorbitol to isosorbide and finds that $NbOPO_4$-pH2 with the highest acid amount shows the best performance and is used in the sequential process. The reaction conditions (especially reaction temperature and reaction time) are systematically investigated and 56.7% isosorbide yield is obtained under optimal conditions, which is impressive compared with other systems reported with homogeneous or semi-heterogeneous catalysts. This effective catalytic system avoids the use of liquid acid and exhibits excellent cycling stability.

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1. Introduction

Continuing questions about the longevity and stability of petroleum supplies, as well as the environmental impacts of its production and use, have driven the development of alternatives such as agricultural or woody biomass [1,2]. Cellulose is the most abundant source of biomass, and is expected to have a potential ability to become an alternative to fossil resources for sustainable production of chemicals and fuels for preventing global warming by decreasing atmospheric CO_2 generated from the consumption of fossil fuels [3,4]. So, many efforts have been devoted to the development of a green and effective process for cellulose conversion and a range of industrially important chemicals have been synthesized from cellulose, including fermentation with enzymes to produce ethanol [5], thermo-pyrolysis to bio-oils [6] and syn-gas [7], hydrolysis with solid acid to yield glucose [8], 5-hydromethylfurfural (HMF) [9] and levulinic acid (LA) [10]. Recently, the biomass-derived polyols such as sorbitol are being considered as new bio-based platform molecules from cellulose valorization, which were firstly reported by Fukuoka and Dhepe [11]. They found that over Pt/Al_2O_3 bifunctional catalyst, 31.0% yield of hexitols (including sorbitol and mannitol) can be obtained from cellulose under optimum conditions [11]. After then, lots of works have been conducted aiming to develop more efficient solid catalysts, such as Ru/C, Ru/CNT, and $Ru/Cs_3PW_{12}O_{40}$ [12]. Interestingly, transition metal carbide catalysts were reported to be highly active for the production of ethylene glycol from cellulose [13], and high yield of 1,2-propanediol (30.7%) and ethylene glycol (75.4%) could be obtained. However, the active sites of the catalysts and the underlying mechanism of the C—C bond cleavage remain unclear.

Isosorbide is a promising platform molecule and has very important applications in many fields, for example, as a pharmaceutical intermediate, as additive to enhance the strength and rigidity of polymers, and as a monomer for biodegradable polymers [14]. The acid-catalyzed dehydration of sorbitol to isosorbide has been subjected to extensive research both in academia and industry [15]. Currently, several solid acid catalysts, such as CuSO-650, and metal (IV) phosphates have attracted much attention and used as potential catalysts for isosorbide production from sorbitol due to their environmentally friendly natures with respect to lower corrosiveness, less waste and easy separation and recovery [16]. In 2010, Moulijn et al. reported the feasibility of converting cellulose to isosorbide in molten salt hydrate media [17]. However, the

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separation and purification steps of intermediate were necessary in this system. Very recently, several catalytic systems were proposed for a one-pot reaction from cellulose to isosorbide with binary catalysts composed of HCl or heteropoly acid and Ru/C, and high yields of isosorbide were obtained [18,19]. However, liquid acid or soluble heteropoly acid was used and the catalyst showed inferior stability in both processes. So more environmentally benign systems are desirable.

Mesoporous niobium phosphate ($NbOPO_4$) has been well studied as a strong solid acid in our group and used for the dehydration of fructose to HMF, hydrolysis/hydrogenation of cellulose to sorbitol as well as hydrodeoxygenation of furan-based compounds to liquid alkanes [20–22], in the latter two novel metals were used as co-catalysts. Herein, we continued our work to the direct conversion of cellulose into isosorbide over mesoporous niobium phosphate ($NbOPO_4$)-based heterogeneous catalysts via a sequential process based on its strong acidity. Cellulose was firstly hydrolyzed to glucose and then hydrogenated to sorbitol over a bifunctional 5 wt.% Ru/$NbOPO_4$-pH2 catalyst under mild conditions as we reported in previous work [21]. Then the catalyst was filtered off and $NbOPO_4$-pH2 catalyst was added to the reaction mixture (mainly including sorbitol and sorbitan) directly for further dehydration to isosorbide via sorbitan isomers. It was reported that only 1,4- and 3,6-sorbitan isomers could be further dehydrated to isosorbide, while 1,5- and 2,5-sorbitan isomers were stable and unable to undergo a second dehydration [23]. In this system, the use of liquid or soluble acid was avoided, and the separation and purification of intermediates were also not needed.

2. Experiment

Microcrystalline cellulose powder (PH-101) was provided by Fluka. Sorbitol was purchased from Shanghai Linfeng Chemical Reagent Co. Ltd. ZSM-5 was purchased from Nankai University Catalyst Co. Ltd. γ-Al_2O_3 was provided by BASF Chemical Company. All other chemicals were of analytic grade which were used directly without further purification. The $NbOPO_4$-based catalysts (including Ru/$NbOPO_4$-pH2 and $NbOPO_4$-pH2) were prepared according to our previous methods [20,21].

2.1. Synthesis of catalysts

The synthesis of mesoporous niobium phosphate at different pH values was according to our previous work [20,21]. In a typical synthesis, 1.32 g (0.01 mol) of diammonium hydrogen phosphate was dissolved in 20 mL water and then adjusted to pH 2 using phosphoric acid. With vigorous stirring, 20 mL of 0.5 M niobium tartrate (pH 2) was added to the above solution. Then the mixed solution was dropped into the aqueous solution of cetyltrimethyl ammonium bromide (CTAB), which was previously prepared by dissolving 1.0 g of CTAB in 13 mL of water. The pH value of the final solution was about 2. Afterwards, this mixture was stirred for additional 60 min at 35 °C, and then the solution was aged in a Teflon-lined autoclave for 24 h at 160 °C. After cooled down, the solid was filtered, washed with distilled water and then dried at 50 °C. Finally, $NbOPO_4$-pH2 sample was obtained by calcination at 500 °C for 5 h in air to remove organic species. Similarly, another two $NbOPO_4$ samples were also synthesized using the above mentioned approach, but with different initial pH values. Taking $NbOPO_4$-pH7 catalyst for example, diammonium hydrogen phosphate and niobium tartrate were just mixed together. And for $NbOPO_4$-pH10 sample, diammonium hydrogen phosphate and niobium tartrate were adjusted to the pH value of 10, respectively, by using aqueous ammonia, and then mixed together to serve as precursor. Other treatments were the same as $NbOPO_4$-pH2 sample.

The Ru/$NbOPO_4$-pH2 catalyst was prepared by incipient wetness impregnation method [21]. Firstly, the water adsorption of $NbOPO_4$-pH2 was measured. Based on that, The Ru/$NbOPO_4$-pH2 catalyst was prepared by impregnating the supports with calculated amount of aqueous solution of 37 wt.% $RuCl_3 \cdot 3H_2O$ (Ru/$NbOPO_4$ = 5 wt.%). After dried in air overnight, the obtained sample was directly reduced ex situ in a fixed-bed flow reactor with pure hydrogen (30 mL/min) at 400 °C for 2 h.

2.2. Characterization

Nitrogen adsorption/desorption isotherms were measured at 77 K on an ASAP 2010 analyzer (Micromeritics Co. Ltd.). Before the measurements, all samples were outgassed at 180 °C for 12 h under vacuum to remove moisture and impurities. BET method was used to calculate the surface area.

Infrared (IR) spectra of pyridine adsorption were recorded on a Nicolet NEXUS 670 FT-IR spectrometer, with 32 scans at an effective resolution of 4 cm^{-1}. The samples were pressed into self-supporting disks (13 mm diameter, 50 mg) and placed in an IR cell attached to a closed glass-circulation system. The disk was pretreated by heating at 400 °C for 1 h under vacuum in order to remove physisorbed impurities. After the cell was cooled down to room temperature, the IR spectrum was recorded as the background. Pyridine vapor was then introduced into the cell at room-temperature and heated to 200 °C until equilibrium was reached, and then a second spectrum was recorded. The spectra presented were obtained by subtracting the spectra recorded before and after pyridine adsorption. To calculate the amount of Brönsted/Lewis acid sites, the acidic site densities were quantified from Py-FTIR spectra using the method proposed by Lachter et al. [24] by using the following expressions.

$$C_L = K_L \times A_{1440} = \frac{\pi}{\mathrm{IMEC_L}} \times \left(\frac{r^2}{w}\right) \times A_{1440}$$

and

$$C_B = K_B \times A_{1540} = \frac{\pi}{\mathrm{IMEC_B}} \times \left(\frac{r^2}{w}\right) \times A_{1540}$$

where C_L and C_B are concentrations of Brönsted acid sites and Lewis acid sites in μmol g^{-1}; A_{1440} and A_{1540} are integrated areas of bands at 1440 and 1540 cm^{-1}; K_L and K_B are molar extinction constants for Brönsted acid sites and Lewis acid sites, respectively; $K_i = \pi/\mathrm{IMEC}_i \times (r^2/w)$; $\mathrm{IMEC_L}$ and $\mathrm{IMEC_B}$ are integration molar extinction coefficients, 2.22 and 1.67 cm μmol^{-1}, respectively, r is the wafer radius in cm, and w is the wafer weight in g.

The number and strength of acidic sites in $NbOPO_4$-pH2 and Ru/$NbOPO_4$-pH2 were also determined by the non-aqueous titration on a potentiometric titration meter (ZDJ-5, Shanghai Lei ci Instrument Factory) as described in reference [25]. Typically, 0.10 g of solid sample was suspended in 25 mL of acetonitrile and agitated for 3 h. Then, the suspension was titrated with 0.026 mol/L n-butylamine in acetonitrile at a rate of 0.1 mL/min. The electrode potential variation was measured with a manual continuous titration model using a double junction electrode. The addition continued until no further change of mV was recorded.

2.3. Catalytic reactions

The ball-milled cellulose sample was prepared using a laboratory ball mill (QM-3SP04). To get desired sample, about 2 g of microcrystalline cellulose was charged into the grinding cell and the ball milling was operated at a frequency of 50 Hz with 6 mm agate balls for 10 h.

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