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Efficient conversion of cellulose into 5-hydroxymethylfurfural over niobia/carbon composites

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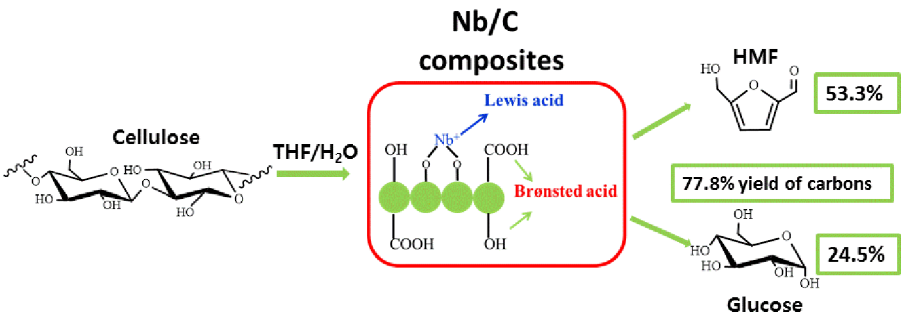
HIGHLIGHTS

- Niobia/carbon (Nb/C) composites are active in the conversion of glucose to HMF.
- As high as 53.3% yield of HMF with 24.5% yield of glucose are achieved from cellulose.
- The catalyst has excellent stability and was used for eight cycles without deactivation.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of novel niobia/carbon composites were synthesized by hydrothermal method following by carbonization with niobium tartrate and glucose as precursors, and used in the conversion of glucose and cellulose to 5-hydroxymethylfurfural (HMF). These catalysts were characterized by XRD, SEM, TEM, N_2 adsorption/desorption, NH_3-TPD and Py-FTIR techniques and the results showed that the Nb/C catalysts were agglomerated particles, with weak to medium acid strength and suitable Brønsted/Lewis acid sites. When used in the hydrolysis and dehydration of cellulose, as high as 53.3% yield of HMF was achieved over Nb/C-50 catalyst at 170 °C for 8 h, accompanied with 24.5% glucose, with the total conversion of cellulose, indicating the high carbon yield and excellent activity. Furthermore, this catalyst showed excellent recyclability and its catalytic activity still maintained after 8 cycles.

1. Introduction

Biomass shows potential as an alternative feedstock to fossil resources for a variety of chemicals and fuels, moreover, the utilization of non-food biomass has attracted world-wide interests, especially for cellulose which is the most abundant inedible biomass [1,2]. Cellulose is a polymer composed of glucose units linked by β-1,4-glycosidic bonds, and its catalytic conversion to valuable platform chemical has been recognized as a bottleneck in the full use of non-food biomass [3]. One of the attractive routes is the hydrolysis and dehydration of cellulose to produce platform chemical, 5-hydroxymethylfurfural (HMF), because HMF has been considered as a promising candidate for achieving a significant production of high value-added chemicals and biofuels [4,5]. Many considerable efforts have been focused on the direct conversion of cellulose to HMF, but this process is challenging for three tandem steps: hydrolysis of cellulose to glucose, isomerization of glucose to fructose [6–9], and the dehydration of fructose to HMF, which all need the acidic catalyst with suitable acidity to prevent the formation of by-products, such as humins in the acid catalysis

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process. Therefore, it is urgent to develop a reaction system for the efficient production of HMF from cellulose.

Many attempts have been made to investigate homogeneous catalytic routes for HMF synthesis from cellulose [10–14]. Zhang et al. [10] reported $CuCl_2$ and $CrCl_2$ catalyzed transformation of cellulose and 58% HMF was achieved in ionic liquid ([EMIM]Cl). Kim et al. [11] also reported the formation of 58% HMF from cellulose using $CrCl_2$ and $RuCl_3$ as catalyst in ionic liquid ([EMIM]Cl). The above reported homogenous acid showed good performance for production of HMF from cellulose, but it included environmental pollution risk, high cost for separation process and equipment corrosion.

To avoid using corrosive liquid acid and minimize the use of expensive ionic liquids, a new way to effectively solve this problem is the use of solid acid catalysts. Examples of solid acid catalysts used for cellulose hydrolysis and dehydration to HMF include heteropolyacid [15], Sn-Mont [16], zeolites [17,18] and metal oxides [19]. For example, Zhao et al. [15] reported that 52.7% HMF yield was achieved with 77.1% cellulose conversion by using heteropolyacid (HPA) $Cr[(DS)H_2PW_{12}O_{40}]_3$ as catalyst, however, the leaching of catalyst during reaction might limit its application. Wang et al. [16] found that Sn-Mont catalyst was efficient for the conversion of glucose to HMF (53.5% yield), but the conversion of cellulose is quite challenging, with the limitation of 39.1% HMF yield. Nandiwale et al. [17] found that 46% yield of HMF with 67% cellulose conversion can be achieved over Bimodal-HZ-5 zeolite, which was obtained by post-synthesis modification of H-ZSM-5 with desilication. Although Bimodal-HZ-5 zeolite exhibited good yields of HMF, its low hydrothermal stability led to the catalytic activity decreased with four runs. Therefore, it is highly demanded to develop efficient heterogeneous acids with high hydrothermal stability that can be used as catalysts for the conversion of cellulose into HMF.

Recently, Katz's group [20] reported that the carbon catalyst (the post-synthetic surface functionalization of MSC-30) with a high local density of weak-acid sites could effectively catalyze the hydrolysis of crystalline cellulose to glucose and as high as 70% yield of glucose with 96% selectivity would be achieved. However, tiny HMF (<0.1%) was found due to the lack of Lewis acidity. Mu et al. [21] reported the preparation of niobium phytate and found this catalyst had excellent catalytic efficiency and high stability in conversion of fructose to HMF. Meanwhile, Xiong et al. [22] used deposition precipitation-carbonization (DPC) method to prepare niobia/carbon catalysts and high yield of HMF was obtained from glucose conversion over Nb/CB-1-DP catalyst. Moreover, our previous study [23,24] showed that niobia and niobium phosphate had Lewis and Brønsted acidity, as well as high hydrothermal stability and can also be used for glucose and fructose conversion. The hydrothermal stability was possibly come from the NbO_4 species which can be treated as water-tolerant Lewis acid sites [25]. Therefore, we report here the synthesis of amorphous niobia/carbon composites with weak to medium acidity and suitable Brønsted/Lewis acid sites, then used for the conversion of cellulose with high stability. The efficiencies of different Nb_2O_5 contents catalysts toward the production of HMF were compared by studying the acidic features of the catalysts.

2. Experimental

2.1. Materials

Glucose (99.8%), p-toluene sulfonic acid (99.5%) and tetrahydrofuran (THF) were purchased from Shanghai Chemicals Company. 5-Hydroxymethylfurfural (HMF) was purchased from Alfa Aesar Chemical Reagent Company. Microcrystalline cellulose powder (PH-101) was purchased from Fluka Analytical Co. Ltd. All bought chemicals were of analytical grade and used without further purification. The ball-milled cellulose samples were prepared by using a laboratory ball mill (QM-3SP04). To get desired sample, about 2 g 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 12 h.

2.2. Catalyst preparation

Nb/C catalysts with different Nb_2O_5 content were prepared by hydrothermal method and denoted as Nb/C-M (M = 20–65, wt% of Nb_2O_5). The Nb_2O_5 content was measured with TGA analysis and the data are collected in Table 1. In a typical synthesis of Nb/C-50 catalyst, 4 g glucose, 6 g p-toluene sulfonic acid and 1 g citric acid were mixed and dissolved in 30 ml water with adding 10 ml of 0.5 mol/L niobium tartrate [23], then placed in 100 mL Teflon-lined stainless steel autoclave. Subsequently, the autoclave was put into an oven of 180 °C and aged for one day. Then the resulting dark powder was collected, washed with hot water and dried at 100 °C overnight. Finally, the carbonation process was carried out in a N_2 flow of 30 $cm^3\ min^{-1}$ at 500 °C and held for 4 h. Nb/C-20, Nb/C-35 and Nb/C-65 were prepared by using the same method except adding different amount of niobium tartrate, 2, 5 and 15 ml, respectively.

2.3. Characterization

Thermogravimetric analyses (TGA) was performed with PerkinElmer Pyris Diamond TG/DTA using air as the purge gas with a heating rate of 10 °C/min. The flow rate of purge gas was always 50 mL/min. Powder XRD patterns were recorded on a Bruker diffractometer (D8 Focus) by using Cu Kα (λ = 0.154056 nm) radiation. The nitrogen adsorption measurements were performed on a Micrometrics ASAP 2020 M sorption analyzer. The BET method was used to calculate the specific surface area.

Ammonia temperature-programmed-desorption (NH_3-TPD) was carried out in a PX200 apparatus (Tianjin Golden Eagle Technology Limited Corporation) with a thermal conductivity detector (TCD). The catalyst (100 mg) was charged into the quartz reactor, and the temperature was increased from room temperature to 600 °C at a rate of 10 $°C\ min^{-1}$ under a flow of N_2 (40 $ml\ min^{-1}$), and then the temperature was decreased to 90 °C. Finally, NH_3 was injected into the reactor at 90 °C under a flow of N_2 (40 $ml\ min^{-1}$). When the adsorption saturation was reached, followed by a flow of N_2 for 1 h at 90 °C, then the temperature was increased from 90 °C to 600 °C at a rate of 10 $°C\ min^{-1}$ and the amount of desorbed ammonia was detected by using thermal conductivity detector (TCD) at 110 °C. Besides, a blank measurement was conducted without adsorption of ammonia and after deducted the blank measurement, the NH_3-TPD curve of catalysts were obtained.

Infrared (IR) spectra of pyridine adsorption were recorded on Nicolet NEXUS 670 FT-IR spectrometer. The samples were pressed into self-supporting disks and placed in an IR cell attached to a closed glass-circulation system. The disk was dehydrated by heating at 400 °C, for 1 h under vacuum in order to remove the

Table 1
Summary of physicochemical properties of Nb/C composites.

Sample	Surface area /$m^2\ g^{-1}$	Pore volume /$cm^3\ g^{-1}$	Nb_2O_5 content /wt.%[a]
Nb/C-20	323.7	0.17	19.8
Nb/C-35	342.1	0.19	36.2
Nb/C-50	376.6	0.29	51.2
Nb/C-65	384.1	0.31	67.4

[a] Nb_2O_5 loading was determined TGA analysis.