



Research Paper

Hydrothermally stable Nb-SBA-15 catalysts applied in carbohydrate conversion to 5-hydroxymethyl furfural

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ABSTRACT

5-hydroxymethyl furfural (HMF) is a bio-based platform chemical with high potential. The as-synthesized Nb-SBA-15 catalysts with mesoporous structures showed high catalytic performance for the conversion of carbohydrates to HMF in a “one-pot” process using biphasic conditions of THF/H₂O–NaCl as the solvents. Nb-SBA-15 catalysts with different Si/Nb ratios were characterized by analytical techniques such as XRD, elemental analysis, SEM, TEM, N₂ adsorption, NH₃-TPD UV–vis DRS, Raman and Pyridine-FTIR. It was found that the acidity of Nb-SBA-15 catalysts could be tuned by modifying addition amount of niobium. The effects of reaction conditions, including temperature, time, and catalyst loading, on the conversions of carbohydrates and the yields of HMF were also investigated. The studies showed that Nb-SBA-15-40 catalysts which Si/Nb ratio is 40 gave the best yields of HMF due that Nb-SBA-15-40 had more niobium species in the SBA-15 silica framework and the mononuclear tetrahedral NbO₄. Under the optimized conditions, the yield of HMF could reach 61.8% at 93.5% glucose conversion and 50.7% at 94.0% cellulose conversion, respectively. Moreover, its catalytic performance was largely retained after 10 recycles in glucose conversion reaction vindicating its good catalytic stability.

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Introduction

It is well accepted that present petroleum based chemicals need to be replaced with renewable resources because of a rapidly rising global population and the dwindling reserves of petroleum based chemicals [1–4]. Therefore, effective utilization of renewable bio-based resources for the production of platform chemicals is ineluctable and necessary. One of the most important productions from carbohydrate is 5-hydroxymethylfurfural (HMF) that is a bio-based platform chemical with high potential [5–7]. HMF serves as a promising candidate to achieve a wide variety of high value-added intermediates (e.g., dihydroxymethylfuran [8], dimethyl furan [9] and levulinic acid [10]).

Based on the previous research [11], it is found that the process of converting glucose to HMF includes tandem steps (Fig. 1). The first step of glucose isomerization is catalyzed in the presence of bases, enzymes, or Lewis acids. Brønsted acids drive the second step of fructose dehydration to HMF.

Up to now, various catalysts have been developed for the production of HMF from dehydration of glucose, which can be divided into two categories: homogenous catalyst and heterogeneous cat-

alyst. Homogenous catalysts include ionic liquids [12], lanthanide salts in ionic liquids [13] and metallic salts with mineral acids [14]. It is well-known that the disadvantages of homogenous catalysts include the equipment of corrosion, catalyst waste and difficult separation operations. And ionic liquids are expensive. Therefore, their replacement by heterogeneous catalysts especially solid acids is highly recommended owing to their environmentally friendly character, the easier catalyst recyclability, and product separation and recovery steps. Lu et al. [15] synthesized partially hydroxylated AlF₃ using a sol-gel method. This catalyst could get 95.5% of glucose conversion and 57.3% of the optimized yield of HMF within 10 h at 140 °C. But catalyst recycling could not perform well. Only in three runs, HMF yield and glucose conversion decreased from 57.3% to 45.6% and 95.5% to 89.3%, respectively. Jimenez-Morales et al. [16] prepared Al-MCM-41 catalyst by a sol-gel method with *n*-dodecylammonium chloride as the template. It exhibited excellent activity in the dehydration of glucose to HMF in a biphasic condition of MIBK/H₂O (98% of glucose conversion and 63% of HMF yield). However, the catalyst activity decreased with three runs (glucose conversion from 98% to 88%, HMF yield from 63% to 45%). It can be seen that the reported catalysts are hard to keep excellent hydrothermal stability. Therefore, it is highly demanded to develop a hydrothermal stable catalyst that can be used for the conversion of carbohydrate to HMF with multiple times.

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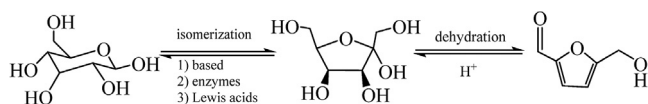


Fig. 1. Synthesis process of HMF from glucose.

Niobic acid is a well-known water-tolerant solid acid as a potential solid acid candidate in water [17–20]. It is a very promising catalyst for dehydration of glucose in THF/H₂O biphasic reaction system [21]. Zhang et al. [22] found that mesoporous niobium phosphate exhibited high activity in the dehydration of glucose to HMF in biphasic phase which gave 68.1% glucose conversion with 33.2% HMF yield at 160 °C. Based on these, we designed a niobium-based mesoporous material which was used as the more efficient and environmental friendly catalysts for the production of HMF. This catalyst not only has good hydrothermal stability but also moderate acidity and good pore structure [23].

Among many kinds of mesoporous materials, ordered mesoporous material of SBA-15 which has a hexagonal pore structure has received much attention in the past decades [24,25]. This could owe to unique nature of SBA-15 which has a large pore channel network with easy and direct access for substrate and product. Thus the unique structure of SBA-15 could promote the inclusion or diffusion throughout the pore channels without pore blockage. Such properties spur the prospective utilization as catalysts and adsorbents [26–28]. On the other hand, niobium-based materials have been widely applied in catalyzing various types of reactions such as oxidation, dehydration, epoxidation [29–31]. Modification of the mesoporous silica by niobium leads to formation of Nb-containing mesoporous silica with isolated and tetrahedral coordinated Nb-oxide species [32,33].

Visualizing the above mentioned superior nature of SBA-15, we explored Nb incorporated SBA-15 for the dehydration of glucose to HMF in biphasic system of THF/H₂O–NaCl. Nb was incorporated into SBA-15 by a conventional hydrothermal synthesis. The acidity of Nb-SBA-15 was tuned by incorporating different Nb levels in the samples to study the acidity effect on the reaction. Detailed characterization of the synthesized materials was investigated in the reaction of glucose in biphasic system to find the optimal catalysis conditions. We also studied various process parameters to achieve the best dehydration reaction conditions.

Experimental section

Chemicals

5-Hydroxymethylfurfural (HMF) was purchased from Alfa Aesar Chemical Reagent Company and cellulose from Fluka Analytical Co. Ltd., Niobium tartrate as precursor was home-made according to the literature [22,34]. The other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. All purchased chemicals were analytical grade and used without further purification.

Material preparation

In a typical synthesis process [35,36], 2.0 g of P123 was dissolved in 50 ml of 1 M HCl aqueous solution at 35 °C. When P123 was dissolved completely, 4.5 g of tetraethyl orthosilicate (TEOS, 98%) was added with stirring. The resulting mixture was stirred for 6 h at 35 °C. Then, a required amount of niobium tartrate dissolved in 30 ml of 1 M HCl aqueous solution was added to the pre-hydrolyzed silicate sol. After further stirring for 24 h at 35 °C, the mixture was transferred into a Teflon-lined autoclave for crystallization at 100 °C for 3 days. The products were filtered with washing by deionized water and ethanol, dried at 100 °C overnight and calcined in

air at 550 °C for 5 h with a ramp rate of 2 °C/min to remove the template. By varying the amount of niobium tartrate, a series of Nb-SBA-15-*n* (*n* indicates the molar ratio of Si/Nb) catalysts were prepared. As comparison, Nb₂O₅/SBA-15 (the molar ratio of Si/Nb is 40) was prepared by impregnation method.

Characterization

Low-angle X-ray diffraction patterns were collected in the 2θ range 0.5–5°, with a Philips X'pert Pro diffractometer using Ni filtered CuK_α radiation (*k* = 1.5406 Å, 40 kV, 30 mA), at a scan rate of 0.5° min^{−1}.

Nitrogen adsorption-desorption isotherms of the catalysts were measured at −196 °C on a Micromeritics ASAP 2020 M sorption analyzer. Prior to the measurements, the samples were heated in a vacuum at 373 K for 8 h to remove moisture and volatile impurities. The surface area was calculated by Brunauer–Emmett–Teller (BET) method on basis of the desorption data. The pore size distribution was calculated by Barrett–Joyner–Halanda (BJH) method. The total pore volume (*V_t*) was estimated at a relative pressure of 0.95.

Scanning electronic microscopy (SEM) images were obtained from JEOL JSM-63602 V and Hitachi S-3400N microscopes operated at 5 kV or 15 kV, respectively. Transmission electron microscopy (TEM) images were captured using a FEI Tecnai G2 F20 S-TWIN instrument at 200 kV. The actual niobium concentration in the samples was determined using the ICP-AES instrument by digesting in a HF and H₂SO₄ mixture.

Ammonia temperature-programmed-desorption (NH₃-TPD) was carried out in a PX200 apparatus (Tianjin Golden Eagle Technology Limited Corporation) equipped with a thermal conductivity detector (TCD). About 50 mg of the sample was heated at 550 °C for 1 h in N₂ flow (40 ml min^{−1}) to remove adsorbed water. When cooling down to 90 °C, ammonia was saturated followed by N₂ (40 ml min^{−1}) purge for 1 h. The samples were then heated to 500 °C with a rate of 10 °C min^{−1} and the amount of desorbed ammonia was detected by using a thermal conductivity detector (TCD) at 110 °C [22].

UV–vis diffuse reflectance spectra (UV–vis DRS) were measured with a Perkin-Elmer Lambda 950 spectrometer equipped with a Praying-Mantis diffuse reflectance attachment. BaSO₄ was used as a reference.

Raman spectra of samples were collected on a Raman microscope (LabRAM HR, Horiba J.Y.) equipped with a deeply depleted thermoelectrically cooled CCD array detector and a high-grade Leica microscope (long working distance objective 50×). A visible 514 nm argon ion laser with 10 mW was used for an excitation.

Infrared (IR) spectra of the pyridine adsorption were recorded on a Nicolet NEXUS 670 FT-IR spectrometer, with 32 scans at an effective resolution of 4 cm^{−1}. 50 mg of a sample was pressed into a self-supporting wafer. The disc was mounted in a quartz IR cell equipped with a CaF₂ window and a vacuum system. Prior to adsorption, the samples were pretreated at 400 °C under vacuum, then cooled to 50 °C when pyridine vapor was introduced into the cell. The samples were heated in vacuum at 100 °C, 200 °C and 400 °C, respectively and spectra were recorded at room temperature. The quantification of acid sites was performed using the same expressions as those in the article of Rocha et al. [37,38]:

$$C_L = K_L A_{1450} = \frac{\pi}{\text{IMEC}_L} \left(\frac{r^2}{w} \right) A_{1450}$$

$$C_B = K_B A_{1540} = \frac{\pi}{\text{IMEC}_B} \left(\frac{r^2}{w} \right) A_{1540}$$

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