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An efficient and heterogeneous recyclable silicotungstic acid with modified acid sites as a catalyst for conversion of fructose and sucrose into 5-hydroymethylfurfural in superheated water

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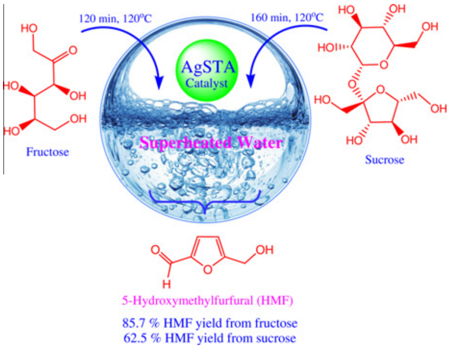
HIGHLIGHTS

- Acidity modified silver exchanged silicotungstic solid acid catalyst was prepared.
- Activity of AgSTA was evaluated for the dehydration of sugar in superheated water.
- 98% fructose conversion and 85.7% HMF yield was obtained at 120 °C in 120 min.
- 92% sucrose conversion with 62.5% of HMF yield was obtained using 10 wt.% of AgSTA.
- The AgSTA catalyst was separated by filtration process and reused eight times.

GRAPHICAL ABSTRACT



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ABSTRACT

Acidity modified silver exchanged silicotungstic acid (AgSTA) catalyst was prepared and characterized by X-ray diffraction, FT-IR spectroscopy, Raman spectroscopy, FT-IR pyridine adsorption, SEM imaging, EDX mapping, and antimicrobial activity was also tested. The catalytic activity was evaluated for the dehydration of fructose and sucrose in superheated water. As a result, 98% conversion of fructose with 85.7% HMF yield and 87.4% HMF selectivity in 120 min reaction time at 120 °C reaction temperature using 10 wt.% of AgSTA catalyst was achieved. While, 92% sucrose conversion with 62.5% of HMF yield was obtained from sucrose at uniform condition in 160 min. The effect of reaction parameters, such as reaction temperature, time, catalyst dosage, and effect acidity on HMF yield was also investigated. The AgSTA catalyst was separated from the reaction mixture by filtration process at end of the reaction and reused eight times without loss of catalytic activity.

1. Introduction

Diminishing fossil fuel reserves and growing attention about global warming are indicates that sustainable sources of energy and fine chemicals will need to be developed. Biomass resources are promising alternatives for the sustainable supply of biofuel and related valuable fine chemicals (Corma et al., 2007). Especially, carbohydrates derived from biomass, which are abundant, relatively inexpensive and renewable promising energy sources for synthesizing a broad range of bio-based platform chemicals (Wua et al., 2012). Among current biofuel sources, 5-hydroymethylfurfural (HMF) derived from carbohydrate is a versatile and key intermediate that is attracting much attention in biofuel chemistry and in the petroleum industry. Moreover, sugars such as fructose, sucrose, and glucose have been shown to be the preferred feedstock for a high yield

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production of HMF (Corma et al., 2007). In last two decades, much effort has been devoted for the development of sustainable methods for the preparation of HMF from sugar (Corma et al., 2007). The most convenient method for the preparation of HMF is the acid catalyzed dehydration of sugar, and this process has received privileged position in sugar conversion (Zhou et al., 2011).

The dehydration of sugar to form HMF has been conducted in water, organic solvents (DMSO, MIBK), organic/water mixtures, and now a day, biphasic water/organic systems, using various acidic catalysts. Mostly, catalysts such as mineral acids (Chheda et al., 2007), transition metal ions (Shimizu et al., 2009), H-form zeolites (Carlini et al., 1999), and strong acid cation-exchange resins were utilized in these processes. Recently, various catalytic systems including metal halides and ionic liquids were also used for the conversion of sugar into HMF and good to efficient results were obtained (Zhao et al., 2007). In addition, ionic liquids were serving as both solvents and catalysts for the dehydration of carbohydrates into HMF and these reactions were also showed promising results (Tao et al., 2011; Jadhav et al., 2012). Moreover, microwave assisted reactions using acidic catalyst conversion of sugar to HMF have been also reported with high conversion of sugar and good to efficient HMF yield (Serrano-Ruiz et al., 2012).

In contrast, heterogeneous catalysts have been receiving more attention over homogeneous catalysts because of their advantages in easy recovery and recyclability in dehydration of sugar (Corma et al., 2007). In view of this, the solid acidic resin Amberlyst-15 was reported to be able to convert fructose into HMF with 100% yield in DMSO (Shimizu et al., 2009). However, the separation of HMF from DMSO requires high amount of energy to evaporate DMSO (Román-Leshkov et al., 2006). While, more than 80% HMF yield can be achieved in 1-butyl-3-methylimidazolium chloride (BmimCl) catalyzed by Amberlyst-15, in this case the separation of HMF and recycling of the ionic liquid are still two problems to be solved. Furthermore, the sulfated zirconia was proven to be an effective catalyst for producing HMF from fructose in organic solvent but shows poor catalytic activity in water (Qi et al., 2009). However, the high cost of organic solvent and ionic liquids could limit their large scale application in sugar dehydration reaction in these methods. Therefore, there are essential needs for heterogeneous catalyst on high concentration sugar conversion to HMF with both high yield and significant selectivity in environmental benign reaction condition.

Heteropolyacids (HPAs) are known to be efficient acidic catalysts for various organic reactions. Especially, these acid catalysts have a wide range of applications in fine chemical synthesis (Zhu et al., 2011). Nevertheless, its applications are limited in the bulk form as they are soluble in water and polar solvents, possess low surface area, and low thermal stability (Kozhevnikov, 2007). In order to overcome these difficulties HPAs could be modified at a molecular level. Modification of heteropoly acids, particularly the Brønsted acidic sites to Lewis acidic site in Keggin-type is highly beneficial in organic reactions (Kozhevnikov, 1998). In addition, it is also reported that for the dehydration of sugar especially in aqueous media, Lewis acidity is highly favorable than Brønsted acidity in conversion of fructose and sucrose into HMF (Carniti et al., 2011; Deng et al., 2012). The Brønsted acidic protons of HPAs exchanged by large monovalent cations such as Cs^+, K^+ and Ag^+ could form a range of insoluble, microporous solid Lewis acidic catalysts effective in various catalytic reactions (Baba et al., 1983). Among these reactions, dehydration of monosaccharides and disaccharides were also reported using unmodified and modified phosphotungstic acid ($H_3PW_{12}O_{40}$) in water/organic biphasic solvent system and in pure organic solvents (Qu et al., 2012). Despite, the advantage of this catalyst, one critical limitation associated with these reactions is the use of organic solvent as reaction medium which is hazardous considering the environmental point of view.

Superheated water should be a more useful replacement for organic solvents because water is most environmentally acceptable and its physicochemical properties can be changed widely with pressure and temperature (Siskin and Katritzky, 2001). Recently, water, between 100 °C and its supercritical point at 374 °C, is described by different researchers as "Superheated Water" and at temperature from 100 to 220 °C and appropriate pressures were found to be an effective low-polarity solvent and it was employed as a reaction medium in various organic synthesis and in extraction processes (Reardon et al., 1995). Moreover, dehydration of fructose to HMF in sub-critical water was reported in the presence of different laboratory made zirconium phosphate solid acids at 240 °C and obtained 80.9% fructose conversion and 62.1% HMF yield (Asghari and Yoshida, 2006). In addition, niobic acid (Carniti et al., 2006), modified niobic acid and concentrated aqueous $ZnCl_2$ solution were also utilized as catalyst in dehydration of fructose in water and resulted efficient yield of HMF (Deng et al., 2012, Qi et al., 2008). However, these reported methods did not achieve 100% conversion of sugar and highly efficient HMF yield. Therefore, dehydration of sugar could be performed in green solvent such as water using modified acid sites of HPAs as solid heterogeneous catalyst without addition of an organic solvent and metal salt or mineral acid co-catalyst is highly desirable and such process would be safer, cheaper and greener than many of the processes in use today. Herein, we report the silver exchanged silicotungstic acid (AgSTA), as a solid acid catalyst, for the dehydration of fructose and sucrose in superheated water. The alternative aim in the modification of silicotungstic acid is the adaptation of Brønsted acidic sites into Lewis acidic sites and their effect on dehydration of fructose and sucrose in superheated water. Moreover, the influence of various process parameters, such as reaction temperature, reaction time, catalyst dosage, on sugar conversion and HMF yield were investigated and compared with the literature values. Antimicrobial test as well as reusability test of AgSTA catalyst was also determined.

2. Experimental

2.1. Materials

Silicotungstic acid hydrated ($H_4[Si(W_3O_{10})_4]\cdot nH_2O$) (99.0%), silver nitrate ($AgNO_3$) (99.0%), 5-hydroxymethylfurfural (99.0%), levulinic acid (99.0%), formic acid (99.0%), D-fructose (99.0%), sucrose (99.0%), sodium sulfate (99.0%), Pyridine anhydrous (99.8%), potassium bromide (99.0% IR grade), etc. were purchased from Sigma Aldrich. All solvents were purchased from commercial sources and were distilled from the relevant agents prior to use. Deionized water was used for the preparation of aqueous solutions and for the dilution of reaction samples.

2.2. Catalyst preparation

Silver exchanged silicotungstic acid (AgSTA) was prepared using precipitation technique and the representative reaction is shown in Scheme S1 in the Supporting information. In a 100 ml round bottom flask 1.0 mmol of silicotungstic acid (STA) was dissolved in 10 ml deionized water. Then, the required amount of 1 M aqueous solution of $AgNO_3$ was added carefully controlled by using an automatic syringe pump to the former solution with vigorous stirring at room temperature. Initially 2 ml aqueous solution of $AgNO_3$ was added at a rate of 2 ml/h, and then the remaining solution was added at a rate of 10 ml/h. If ones added the aqueous $AgNO_3$ solution to the aqueous solution of $H_4SiW_{12}O_{40}$ at a constant rate of 10 ml/h from the beginning, fine particles with large external surface area were formed, which had adverse effect on the catalytic activity and solubility. Thus, the careful control of the addition of