



Aluminium oxide-silica/carbon composites from rice husk as a bi-functional heterogeneous catalyst for the one-pot sequential reaction in the conversion of glucose



Syed M. Al-Amsyar, Farook Adam*, Eng-Poh Ng

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

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ABSTRACT

A simple preparation of aluminium oxide-grafted silica/carbon composites (Al-SiO₂/C) from rice husk is reported. This composite has been employed as a bifunctional heterogeneous Lewis-Brønsted acid catalyst in the conversion of glucose into 5-hydroxymethylfurfural (HMF). SEM images showed the presence of bulk and nanosized Al-SiO₂/C particles which were closely packed on the catalyst's surface. XPS data proved the presence of Al in the form of aluminium oxide and graphitic carbon with several functional groups. The XRD data confirmed this catalyst was amorphous. The results from N₂ adsorption-desorption isotherm showed Al grafting did not affect its physicochemical properties. Pyridine-probe FTIR verified the existence of Lewis and Brønsted acid sites. A yield of 52% 5-hydroxymethylfurfural (HMF) was obtained at 170 °C in N-methylpyrrolidone (NMP) solvent. The catalyst proved to be stable without significant loss of yield after several recycling experiments.

1. Introduction

The development of catalyst from waste material is gaining prominence due to economic and environmental concern. There are several approaches currently being pursued for the utilization of waste material in catalytic activity. For instance, the waste material are directly used as active materials, as catalysts precursor, as surface-modified materials, and as pre-catalyst [1]. One of the most abundant agricultural wastes is rice husk, produced from the rice milling industry. It consists of lignocellulosic components such as cellulose, hemicelluloses, lignin, and also silica [2].

Basically, silicic acid and water are taken into the plant via the roots from the soil. The growing paddy plant deposits the silicic acid as silica on the rice husks cell wall, on the surface of leaves and stems in the form of silica-cuticle and silica-cellulose double layers. In addition, small and large silica particles exist in the intercellular layers [3,4]. Reports on the utilization of rice husk as silica and carbon source is abundant in literature [5–7].

For example, utilizing silica from rice husk as a catalyst precursor have been demonstrated recently via grafting and sol-gel techniques. Furthermore, addition of surfactant will create pores in the solid structure. Such treatment can increase the surface area of the prepared catalyst. These materials showed good potential as heterogeneous catalysts such as in alkylation, benzylation, degradation of phenol,

oxidation, and esterification [8]. Lignocellulosic components in rice husk can be transformed into carbon material by carbonization under air or N₂ atmosphere. Recently, silica in rice husk has been used as a natural template to synthesize hierarchical porous carbon [9].

However, the direct preparation and use of rice husk as silica/carbon composite is scarcely reported. Due to its hybrid organic-inorganic nature, the silica/carbon composite can be advantageously utilized, especially as heterogeneous catalyst in organic synthesis [10], transparent conductors [11], and solar absorber [12]. The presence of silica can provide durability and thermal stability for heterogeneous catalyst. Besides, the carbon from the lignocellulosic components will have weak Brønsted acid sites which is crucial in some organic reactions [13].

In this era of diminishing petroleum reserves, researchers around the world have made tremendous efforts to reduce the dependency on crude oil by shifting their focus to use biomass as a chemical feedstock [14]. 5-hydroxymethylfurfural (HMF) has been identified as a potential chemical intermediate in biofuel and fine chemicals [15]. The rehydration of HMF will produce levulinic acid (LA), a highly potential feedstock for herbicide, polymers, and petrochemical production [16].

HMF can be obtained from the dehydration of C₆ sugars such as glucose and fructose in which the latter is a more reactive substrate. The glucose enolizes very slowly and the enolization is a rate determining step for the formation of HMF from glucose [17]. The

* Corresponding author.

E-mail addresses: farook@usm.my, farookdr@gmail.com (F. Adam).

intricacy to obtain high selectivity and isolated yields render HMF to become costly and thus restrict its potential as a key chemical platform. However, the use of glucose as a substrate is more attractive due to its lower cost than fructose [18].

The conversion of glucose into fructose involves isomerization aided by Lewis acid on the catalyst. This is followed by dehydration into HMF in the presence of Brønsted acid [19]. Some researchers have reported the utilization of solid acid catalyst to produce HMF from sugar. Zeolite-Y has been tested as heterogeneous catalyst in aqueous glucose solutions [20]. Although quantitative glucose conversion was achieved, but only less than 10% of HMF yield was attained. The presence of levulinic acid, formic acid, and coke deposition were also detected as by-products. Niobic acid, $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, a heterogeneous Lewis acid catalyst has been tested in glucose conversion into HMF in water [21]. The NbO_4 tetrahedral Lewis acid sites on the surface immediately form $\text{NbO}_4\text{--H}_2\text{O}$ adducts in the presence of water. A yield of 12.1% HMF was obtained. However, $\text{Na}^+/\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ without Brønsted acid sites showed a similar yield (12.4%). This indicates the formation of HMF under this catalytic system was catalyzed by Lewis acid site alone.

In order to obtain high conversion and high HMF yield, the use of organic solvents instead of water has been reported. This step could prevent the rehydration process thus eliminating the formation of levulinic acid. The combination of hydrotalcite and Amberlyst-15 as bifunctional acid-base catalyst has been employed in converting glucose into anhydroglucose (levoglucosan) or HMF [22]. Amberlyst-15 was able to dehydrate glucose into anhydroglucose (32%) in a polar aprotic solvents at 100 °C within 3 hours. However, anhydroglucose could not be dehydrated into HMF. The presence of hydrotalcite allowed isomerization of glucose into fructose. Amberlyst-15 was then able to dehydrate fructose into HMF. The highest yield of HMF in this catalytic system was 41% with 72% glucose conversion in DMF solvent. By adding a small amount of water, HMF selectivity increased to 57–64%.

HMF selectivities of over 70% were achieved from glucose using Sn-Beta catalyst and HCl in a biphasic system [23]. In the aqueous phase, isomerization of glucose and dehydration of fructose took place. After that, the HMF will be extracted into the organic phase from the aqueous phase. The addition of inorganic salts have proved to improve HMF partitioning into the organic phase thus, suppressing the undesired-side reactions [24]. The efficiency of the biphasic system also has been reported [25]. They employed Sn-montmorillonite as a bifunctional Lewis-Brønsted acid catalysts by using similar biphasic solvents (THF/ H_2O /NaCl). A yield of 59.3% HMF was reported at 160 °C in 3 hours. The addition of HCl was not necessary since Sn-montmorillonite consists of Lewis acid sites for isomerization and Brønsted acid sites for dehydration.

Herein, a facile method is reported for preparing silica/carbon composites directly from the rice husk. This was followed by grafting with aluminium oxide to act as a bifunctional Lewis-Brønsted acid catalyst in converting glucose into HMF.

2. Materials and methods

2.1. Preparation of the catalyst

The pre-treatment of rice husk (RH) has been described previously [8,26]. The RH was carbonized in a muffle furnace. First the RH was placed in a stainless steel boat and placed inside the muffle furnace. The sample was heated from room temperature (30 °C) to reach the desired carbonization temperature of 400 °C at a heating rate of 5 °C/minute under air atmosphere. The desired carbonization temperature was maintained for another 1 h. This procedure will transform lignocellulosic components in rice husk into graphitic carbon. The resulting sample was labeled as $\text{SiO}_2/\text{C-x}$, where $x = 400$ (carbonization temperature). Other samples were prepared for $x = 350, 450,$ and 500 .

For Al grafting, 0.05 g of aluminium trichloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) was dissolved in 3.0 mL of methanol. A mass of 0.5 g of

the $\text{SiO}_2/\text{C-400}$ was added to the solution and stirred for an hour. The solid was filtered and dried in an oven at 50 °C overnight. Then, the sample was calcined by heating the composite in a muffle furnace under air atmosphere (furnace temperature = 300 °C, duration = 6 h). This process will produce aluminium oxide-grafted silica/carbon, denoted as $\text{Al-SiO}_2/\text{C-400}$. Similarly $\text{Al-SiO}_2/\text{C-350}$, $\text{Al-SiO}_2/\text{C-450}$, and $\text{Al-SiO}_2/\text{C-500}$ were prepared.

2.2. Characterization of the catalyst

The morphology of the catalysts were studied using scanning electron microscopy (SEM, FEI model Quanta FEG 650 with an electron beam resolution of 3.0 nm at 10.0 kV). The elemental mapping was carried out by using EDX which was coupled with SEM (X-Max 50 mm² SDD detectors with a resolution of 127 nm at MnK_α). The distance between sample and pole piece was 10 mm. The local structure of $\text{Al-SiO}_2/\text{C-400}$ was detailed by using X-ray Photoelectron Spectroscopy (XPS), using High Resolution Multi Technique X-ray Spectrometer (Axis Ultra DLD XPS, Kratos).

The surface area and porosity of the catalysts were analyzed by using N_2 adsorption–desorption analysis (Micromeritics ASAP 2020 porosimeter). The samples were initially degassed at 110 °C for 8 h under vacuum prior to being analyzed. The structural information of the catalysts were characterized by powder X-ray Diffraction (Siemens Diffractometer D5000 Kristalloflex, equipped with Cu K_α radiation, $\lambda = 0.154$ nm) with a step size of 0.05° from 10 to 90° (high angle). The voltage supplied was 40 kV with a current of 30 mA.

Pyridine-probe FTIR spectra were recorded using a Nicolet 6700 FT-IR spectrometer. Prior to measurement, the samples were ground and pressed to obtain a wafer (area 2 cm², mass of 11–13 mg) before being introduced into the vacuum IR cell. The samples were then pre-activated under vacuum (10^{-6} mbar) at 200 °C for 1.5 h. The reference spectrum was first recorded after cooling and then pyridine was introduced to the samples at 25 °C for 30 s. The samples were evacuated at 50 °C to desorb pyridine and the spectra were recorded with a resolution of 4 cm⁻¹ and 128 scans accumulation. The thermal properties of the composite were determined by thermogravimetric analysis (TGA) performed using a TGA SDTA851e instrument operating from 30 to 920 °C at 10 °C min⁻¹ under oxygen atmosphere.

2.3. Catalytic reactions

The catalytic testing was carried out by placing the catalyst, substrate, internal standard (biphenyl), and solvent in the Ace pressure tube (Sigma-Aldrich). The reaction mixture was stirred at 700 rpm for a desired time and temperature by using a pre-heated silicone oil bath coupled with temperature sensor. Next, the reaction mixture was filtered before deuterated DMSO solvent was added to the filtrate for NMR analysis. Subsequent calculations and product identification were carried out. For catalyst reuse experiment, the reaction mixture was separated by centrifugation and the supernatant was removed. The catalyst was washed with acetone several times and dried in oven at 100 °C. It was ground to powder before being used in subsequent reactions.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Scanning electron microscope (SEM) – energy dispersive X-ray (EDX) analysis

The SEM images showed bulk $\text{Al-SiO}_2/\text{C-400}$ (Fig. 1a) and closely-packed $\text{Al-SiO}_2/\text{C-400}$ particles spotted on the surface of the cell (Fig. 1b). Further enlargement of this image revealed that the size of closely-packed $\text{Al-SiO}_2/\text{C-400}$ particles was less than 100 nm (Fig. 1c) with EDX analysis confirming the presence of Al, Si, O, and C atoms (Fig. 1d).

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