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Hydrolysis of cellulose over silica-salicylaldehyde phenylhydrazone catalyst

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ABSTRACT

A novel catalyst has been developed toward the production of second generation (2G) biofuels instead of using the expensive enzymes. Salicylaldehyde phenylhydrazone was immobilized onto silica rice husk ash to form a heterogeneous catalyst denoted as RHPHMP. The BET measurements of the catalyst showed that the surface area to be 194 m^2/g with pore size distribution fall within the microporous region. The FT-IR clearly showed the presence of –NH and C=N absorption bands at the expected range. The elemental and EDX analysis of RHPHMP showed the nitrogen is included into the catalyst structure. The RHPHMP was efficient for the hydrolysis of cellulose, with maximum glucose yield over 82% at 140 °C in 14 h. The catalysts were simple in its preparation, stable during the cellulose hydrolysis in addition to repeatedly without a significant loss of its catalytic activity.

1. Introduction

Cellulose is a bioorganic molecule with a long linear chain polymer of several monomeric D-glucose units linked by β-1,4-glycosidic bonds. It is the most abundant organic compound in nature and does exist in the cell wall of plants as complex fibrous carbohydrates [1]. Each cellulose molecule is a straight chain consisting of 1 to 1000 million D-glucose units. Cellulose is very difficult to break down, and therefore cannot directly be used as a food source. Cellulose hydrolysis is a key technology for obtaining sugars from vegetation, such as grasses, agricultural, and wood waste. The cellulose hydrolysis produced reducing sugars which can be converted into a range of important industrial chemicals including ethanol, furfural, levulinic acid, and starting materials for the production of polymers. Cellulose hydrolysis can be achieved by using enzymes [2], ionic liquid, diluting and concentrating acids [3]. In nature, a variety of microorganisms are known for producing a set of enzymes capable of degrading this insoluble polymer to soluble sugars, primarily cellobiose and glucose [4]. Producing second generation bioethanol from dead plant tissue is environmentally friendly technology, but it is also expensive because the process that is used today needs expensive enzymes, and large international companies dominate this market. Recently, a new technique has developed to make 2G biofuels without the use of expensive enzymes [5]. In our laboratory we had developed a completely enzyme-free technique that is not expensive. The technique uses an acid that is made from treated rice husks ash with chlorosulfonic acid. The ashes from burnt rice husks have a high content of silicate, and this is the important compound in the production of the new acid. The silicate particles were paired with chlorosulfonic acid and this made the acid molecules attach themselves to the silicate compounds. The result was an entirely new molecule, the acid $RHSO_3H$, which can replace the enzymes in the work of breaking down cellulose to sugar for the production of 2G biofuels.

Rice husk (RH) is a major by-product of the rice-milling industries and is abundantly available causing disposal problems. Moreover, its 20% approximately ash content comprising of over 95% amorphous silica which has very fine particle size, very high purity, high surface area, and highly porous would make the rice husk utilization systems becoming very economically attractive [6,7]. One important application of silica is the ability to modify

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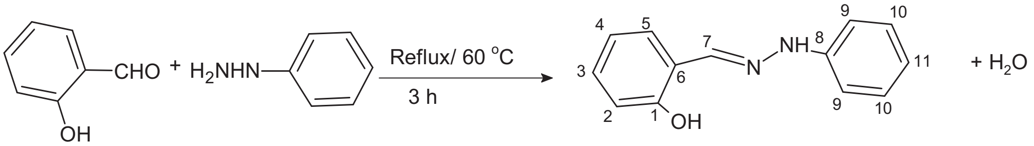

Scheme 1. The synthesis of PHMP. The reaction time and temperature were shown.

with different silylating agents to introduce basic groups through an anchored pendant chain.

Hydrazones have attracted considerable attention due to their interesting chemical and structural properties. Hydrazones are a class of organic compounds with the structure $R_1R_2C{=}NNH_2$. They are related to ketones and aldehydes by the replacement of the oxygen with the $-NNH_2$ functional group. Hydrazone compounds obtained by the reaction of aromatic and heterocyclic hydrazides with mono and di-aldehydes or ketones have revealed very versatile behavior in metal coordination. Many researchers have synthesized a number of new hydrazones because of their ease of synthesis [8,9]. Hydrazones have been studied as a group of the most useful spectrophotometric reagents. The combining of carbonyl compounds and hydrazine, the sensitivity as an analytical reagent and/or solubility of the hydrazones could be improved and the donating environment could be changed [10]. The shortcoming of hydrazones was their lack of selectivity for metal ions. Much effort has been devoted to developing masking agents for use with hydrazones [11]. However, the using of salicylaldehyde phenylhydrazone as a heterogeneous catalyst for the cellulose hydrolysis was not been reported as the best of our knowledge. Here we report the immobilization of salicylaldehyde phenylhydrazone onto silica rice husk ash to make second generation (2G) biofuels catalysis.

2. Materials and methods

2.1. Raw materials

All chemicals were used directly without further purification. These include sodium hydroxide (Systerm, 99%), nitric acid (Systerm, 65%), 3-chloropropyltriethoxysilane (Sigma, 99%), Phenyl hydrazine (BDH, 98%), salicylaldehyde (Hi-media, 98%), toluene (GCC, 98%), ethanol (GCC, 100%), acetone (Sigma, 98%), benzene (Merck, 99%), cellulose (BDH, 98%), lithium chloride (BDH, 98%), dimethylformamide (Riedel-de haen, 99%), ethyl acetate (Hi-media, 98%), DNS reagent (Merck, 98%), triethylamine (Merck, 98%), cyclopentanon (Riedel-de haen, 99%), cyclohexanol (Riedel-de haen, 99%) and butanol (Fluka, 98%). The rice husk (RH) was collected from a rice mill in Kufa, Najaf, Iraq.

2.2. Synthesis of 2-((2-phenylhydrazono)methyl)phenol PHMP

The PHMP was synthesized according to the reported method [12]. In general a 0.02 mol (2.4 mL) of salicylaldehyde was stirred with 10 mL of ethanol for about 20 min and then a 0.02 mol (2 mL) of ethanolic solution of phenyl hydrazine was added gradually to the solution. The mixture was refluxed at 60 °C for 3 h. The reaction was monitoring by TLC using ethyl acetate as an eluent which shows one spot of the product. The yellow product was dried in an oven at 50 °C for 5 h. The product is labeled as PHMP. The reaction was represented in Scheme 1. The yield was 1.61 g (78.0%); m.p: 145 °C; FT-IR: 3450 cm^{-1} (–OH), 3290 cm^{-1}(N–H), 3047 cm^{-1} (Ar–H), 1615 cm^{-1} (C=N); ^{1}H NMR (400 MHz, d6-DMSO) Fig. 1(a): δ 2.4 (1*H*, s, NH), 3.3 (6*H*, s, 2 × CH_3), 6.6–8.2 (9*H*, m, 2 × ArH), 10.3 (1*H*, s, OH), 10.5 (1*H*, s, NH); ^{13}C NMR (400 MHz, d6-DMSO) Fig. 1(b): δ 113.3 (ArC, 2 × C9), 11.5, 120.6, 120.9, 122.0, 139.0 (ArC, C2, C4, C11, C5 & C3), 128.9 (ArC, 2 × C10), 130.8 (ArC, C6), 146.3 (ArC, C8, C7).

2.3. Extraction and modification of silica from RHA

2.3.1. Sources of silica

The RHA was chosen as the source of amorphous silica [13] as it was available in abundance. The silica was extracted from RH according to reported method [14,15].

2.3.2. Synthesis of RHPHMP catalyst

RHA silica was functionalized with CPTES according to the reported method [16]. The resulting solid, RHACCl, was used as the support to immobilize the PHMP onto the silica surface. RHPHMP was prepared by adding 2.0 g (0.01 mol) of PHMP to the RHACCl (1.0 g) in a mixture of 30 mL of dry toluene and 2.0 mL (0.01 mol) triethylamine (Et_3N). The reaction mixture was refluxed at 110 °C in an oil bath for 44 h. The solid was filtered, and washed with three deferent solvents benzene, ethylacetate and ethanol. The solid was dried at 110 °C for 24 h. Finally, it was grind to produce a

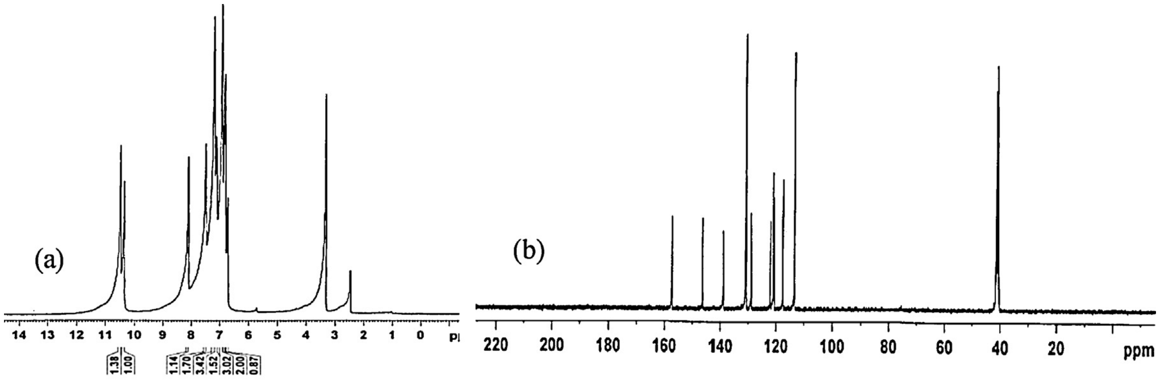

Fig. 1. The ^{1}H and ^{13}C NMR spectra of PHMP using d6-DMSO. (a) ^{1}HNMR and (b) ^{13}CNMR.

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