



Functionalized cellulose-magnetite nanocomposite catalysts for efficient biodiesel production



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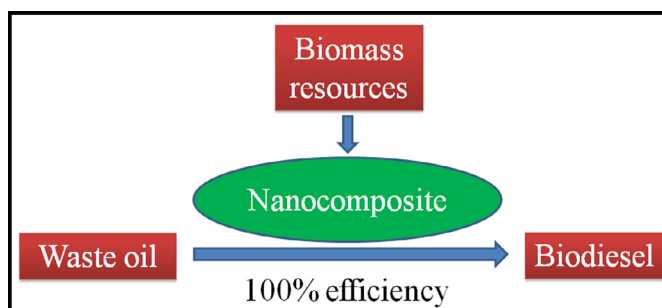
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HIGHLIGHTS

- Cellulose-magnetite nanocomposites were fabricated.
- Nanocellulose was functionalized using different organic and inorganic acids.
- Functionalized nanocellulose derivatives and cellulose-magnetite nanocomposites were characterized.
- The catalytic activity of the fabricated materials was evaluated for esterification.
- Oleic acid and methanol were used for the production of methyl oleate ester (biodiesel).

GRAPHICAL ABSTRACT



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ABSTRACT

Cellulose-magnetite nanocomposites were fabricated *via* the adsorption of magnetite onto the surfaces of functionalized nanocellulose, using different organic and inorganic acids. The properties of functionalized nanocellulose derivatives and cellulose-magnetite nanocomposites were characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray, Fourier transform infrared spectroscopy (FTIR), magnetic properties measurements, and thermal analysis. The catalytic activity of the functionalized nanocellulose and cellulose-magnetite nanocomposites was evaluated towards the esterification of oleic acid with methanol for the production of methyl oleate (biodiesel). The sulfonated cellulose-magnetite nanocomposite (MSNC) showed the highest catalytic activity toward the esterification reaction (96%) due to the high dispersion of the Lewis acid sites resulted from the impregnation of magnetite (0.98 wt%) in addition to the already presented Brønsted acid sites in the surface of the nanocellulose.

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1. Introduction

Esterification is an important organic reaction, where an ester is produced from organic acids and alcohols in presence of a catalyst, which could be an acid catalyst [1]. Esterification and transesterification represent important catalytic processes for biodiesel production via reactions of fatty acids and triglycerides, respectively, with low chain alcohols. Production of biodiesel from edible oil causes a conflict with the food sector but waste vegetable/animal oil and fats are good alternatives and can be obtained at a modest price. However, waste oils must be treated to remove impurities, such as free fatty acids (FFA), before conversion into biodiesel. In this context, biodiesel produced from waste oils and fats can compete with the prices of petroleum diesel.

Homogeneous and heterogeneous acid catalysts have been studied for the esterification of fatty acids, with the commonly used homogeneous acid catalysts are sulfuric and phosphoric acids [2–12]. However, mineral acid catalysts are corrosive. Therefore, they have been replaced by heterogeneous counterparts as green replacements [4], such as zirconia [1], carbon [9], silica [6,13,14], 12-tungstosilicic acid [15] and cellulose [3].

Recently, heterogeneous catalysis has witnessed a great attention. Solid acid catalysts have favorable characteristics such as high selectivity, long catalyst lifetime, ease of recovery and reuse [16], ease of handling, stability at a wide range of temperatures and pressures, and easily separation from reaction mixtures by filtration and centrifugation [17]. Active heterogeneous catalysts based on different bio-polymers such as cellulose [8,18], chitosan [19,4] have been used in heterogeneous catalytic systems.

A significant interest in the synthesis of multifunctional composites is due to the variety of characteristics that may arise from the combination of two or more constituents. Magnetic cellulosic materials have recently been prepared by incorporating iron oxides [20,21], copper iodide [22], cobalt-iron oxide [21] or nickel [23] into the cellulose matrix. Cellulose is a straight chain polymer composed of cellobiose units formed from D-glucose via β -1,4 glycosidic bonds. It consists of amorphous and crystalline regions where the crystalline regions may be utilized to produce nanocrystalline cellulose [24]. Isolation and characterization of nanocrystalline cellulose from various agricultural resources have been reported [25–34]. The disadvantages of nanocellulose are mainly related to its polar and hydrophilic nature, which can be avoided by surface modification [27]. Due to an abundance of hydroxyl groups on the cellulose surface, it can be easily functionalized, for example via acetylation [35], succinylation [36–38], phosphorylation [39–42], silylation [43–47] and doping by different nanoparticles [48–52]. Cellulosic nanocomposites were used in different applications such as capacitors, batteries, solar cells [53], emulsion stabilizer [54], selective adsorbent [38,55–59] and catalysts for organic reactions [22].

In the present work, oleic acid was selected for evaluating efficiency of heterogeneous catalysts in the esterification process as it is the most abundant FFA in plant oil [1,5,6,8–10,13,15]. Synthesis of methyl oleate (biodiesel) by esterification of oleic acid using acid-functionalized nanocellulose derivatives and cellulose-magnetite nanocomposites is reported. The acid-functionalization of nanocellulose was achieved using organic groups (acetate or succinate) and inorganic groups (phosphorylate or sulfonate), followed by doping of magnetite. The fabricated materials showed exceptional performance upon their use for the green biodiesel production.

2. Materials and methods

2.1. Materials

The chemicals used were analytical grade and used without further purification. Hydrochloric acid (37%), acetic acid anhydride (97%), succinic acid anhydride (95%), pyridine (99%), Chlorosulfonic acid (ClSO_3H , 99%), oleic acid (95%) and methanol (99.8%) were from Sigma–Aldrich (USA). Sodium hydroxide (98%) was from Oxford Lab Chemi, India. Hydrogen peroxide (30%) from Merck, U.S. Methylene chloride (99.99%) was from Fisher Scientific, UK. Phosphorous oxychloride (POCl_3 , 99%) was obtained from LOBA chemi, India. Iron (III) chloride (FeCl_3 , 96%) was from S d fine-limited, india. sodium bicarbonate (99.5%) obtained from BRIXWORTH NORTHANTS, U.K. Ascorbic acid (99%) was from SAS chemicals CO., India.

2.2. Preparation of nanocellulose (NC)

Nanocellulose was prepared from rice straw as follows [60]: rice straw was chopped, washed, dried, and milled to powder. Then soaked in NaOH (3% w/w) at room temperature for 24 h. The straw was washed with deionized water, filtered and treated in (13% w/w) NaOH at 121 °C in an autoclave for 4 h. It was bleached in (8% v/v) H_2O_2 at room temperature for 24 h after washing with deionized water till neutrality. Then steeped in HCl (10% w/w) with ultrasonic agitation at 60 °C for 2 h after washing and filtering again. Finally, it was placed in a high shear homogenizer for 15 min to produce nanocellulose.

2.3. Functionalization of nanocellulose

The nanocellulose support (NC) was acid-functionalized with organic or mineral acids as follows:

2.3.1. Acetylated nanocellulose (ANC) and succinylated nanocellulose (SuNC)

Nanocellulose was acetylated and succinylated as described in previously reported works [61–68] with minor modifications. In details, (4 g) nanocellulose was suspended in 200 ml deionized water, and stirred for one hour at room temperature. Adjust the basicity of the suspension at pH 8.0 using NaOH solution (3 wt. %), and then continue the stirring for additional one hour.

2.5% acetic anhydride or succinic acid anhydride was added slowly to the stirred slurry while keeping the range within pH 8.0–8.4 using NaOH solution (3%). The reaction was allowed to proceed for 10 min after completion of acetic or succinic anhydride addition. Then pH of the slurry was decreased to 4.5 with HCl (0.5 N). The acid-functionalized nanocellulose samples were filtered and washed several times with deionized water. Finally, the produced acetylated nanocellulose and succinylated nanocellulose were dried over night at 40 °C.

2.3.2. Phosphorylated nanocellulose (PNC)

Nanocellulose was suspended in 50 ml pyridine and cooled to low temperature (8 °C). Methylene chloride (20 ml) was mixed with POCl_3 (5 ml) and added to the cooled system drop by drop. Then, the mixture was refluxed at 115 °C for 2 h with stirring. The mixture was filtered after the reaction, washed with deionized water, then with 0.1 N HCl and finally with deionized water till neutrality [69,70].

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