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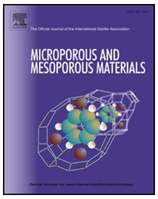

Translation of lignocellulosic waste to mesoporous solid acid catalyst and its efficacy in esterification of volatile fatty acid

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ABSTRACT

The growing environmental concern seeks global attention to minimize the contamination, especially for the disposal of solid wastes. In this preview, a lingocellulosic waste, de-oiled Pongamia pinnata seed cake is converted to a carbonaceous solid by incomplete carbonization and subsequent sulfonation to obtain a mesoporous solid acid catalyst. The physico-chemical properties, surface morphology and molecular structure of the different stages involved in the preparation of the solid acid catalyst was carried out through Elemental analysis, Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy, X-Ray Diffraction, Brunauer-Emmett-Teller (BET) surface area and Thermogravimetric analysis. The characterization results validate the induced catalytic property in the carbonaceous solid with pore diameter of 3.96 nm. The appropriate testification of the catalyst performance was conducted through esterification of lactic acid with n-butanol. In the experimental design based on Taguchi optimization the process parameters catalyst loading, feed molar ratio and temperature effects were investigated. The optimized results suggested a 7 wt % catalyst loading, 1:1.5 molar ratio of acid to alcohol and temperature of 115 °C for the effective conversion of volatile fatty acid. The efficacy of lignocellulosic waste catalyst was compared with other commercial catalysts; sulphuric acid, methane sulfonic acid and Amberlyst-15. Thereby, the study provides an insightful knowledge on the resourceful transformation of a non-edible solid waste precursor to an industrially applicable solid acid catalyst.

1. Introduction

In organic synthesis, liquid phase catalyzed esterification reaction is one of the most important processes that produces intermediates for fine chemicals, drugs, food preservatives, cosmetics [1]. The global catalyst market is estimated to be about $15 billon, more than 35% of the global GDP was associated with catalytic technologies, and 95% of industrial products were estimated to be produced via catalytic processes. The reaction is mainly carried out using homogeneous acid catalyst (sulfuric acid, p-toluene sulfonic acid and phosphoric acid) that are limited with the problems such as corrosion, environmental pollution, side reactions, tedious separation process, less likely catalyst recovery and sensitivity to water [2]. The emergence of sustainable development with the strict environmental norms, heterogeneous acid catalysts have been proposed viz. bronsted acid catalysts, lewis acid catalysts and their mixture [3]. Esterification with solid acid catalyst, including acid zeolites, meso structured silica functionalized with sulfonic groups, tungsten oxide zirconia, sulfonated polymers (Amberlyst-15), and Nafion-based composites has been reported [4]. However, a metal oxide or a zeolite catalyst has low acidic site density and hydrophilic surface. Nafion contain abundant sulfonic acid groups (-SO_3H) that can function as strong acid sites but their catalytic activities are generally much lower due to their very low surface area [2,5,6]. Typically, these large pore acid resins (Nafion and Amberlyst) are more expensive than mineral acid catalysts and restrict the practical utility of acidic cation-exchangeable resins.

Recently, sulfonated carbon solid acid catalysts derived from incomplete carbonization of natural organic material and biomass resources have shown better catalytic performance with high stability for esterification of fatty acids than sulfonated meso-porous silica [6]. Carbon derived materials such as coffee residue [2], rice husk [5], seed shells of karanja [7], wood powder [8], cassava stillage residue [9], corn straw [10], sugar cane bagasse [11], sugar beet pulp [12], canola meal [13] has been used as carbon precursors to prepare solid acid catalyst. The carbon rich material is generally obtained by slow pyrolysis that generate a highly cross-linked, multi ringed aromatic

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structure anchored to lignin [14] that further can be functionalized to make it as strong solid acid catalysts. Nakajima et al. (2007), reports the importance of pyrolysis temperature which is a determining factor on catalytic activity of sulfonated carbon catalysts [15]. Danlin Zeng et al. investigated the performance of sulfonated carbon derived by partial carbonization of natural product viz. sugar, starch for esterification process [5]. The derived material showed less porosity and low surface area as compared to sulfonated mesoporous silica. Thereby, the present research area is primarily focuses on the development a porous, stable, carbonaceous catalyst with high active surface area, high activity, and selectivity in the esterification process from lingo cellulosic waste.

Among the various agro industrial wastes, deoiled Pongamia pinnata seed cake is most abundantly available; with a total output capacity of 200 million tons per year is a potential feedstock for biodiesel in India [16]. Moreover, statistics reveal that about two tons cake of Pongamia pinnata is generated for every ton of biodiesel produced [17]. The generated seed cake is toxic constituting flavonoids, urano-flavonoids, and furan derivatives, making it completely inedible with little or no economic value. Therefore it remains as a solid waste and is utilized in the present study for preparation of a solid acid catalyst to aid simultaneous waste minimization and utilization. Efforts have also been made in prior studies to utilize this seed cake to extract sugars and ethanol [18,19]. Further, the deoiled Pongamia pinnata seed cake has been used as bio-adsorbent for the removal of heavy metals such thorium and zirconium [17,20]. The lignocellulosic waste, seed cake (SC) is subjected to controlled pyrolysis followed by its chemical modification (sulfonation). The derived sulfonated catalyst from seed cake was characterized by elemental analysis, fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), thermo-gravimetric analysis (TGA) and Brunauer Emmett and Teller Analysis (BET).

The catalytic potential of the synthesized catalyst was tested by the esterification of a volatile fatty acid; Lactic acid with n-butanol as an esterification agent to butyl lactate. Moreover, this study is a prerequisite for the recovery of different volatile fatty acids which still remains a major industrial challenge [21]. The experimental matrix for the conversion of carboxylic acid to ester was designed according to Taguchi orthogonal array and process parameters (catalyst loading, molar ratio and temperature) were optimized employing S/N ratio as the objective function. Studies for the stability of prepared catalyst with the recycle runs were also performed. Finally the activity of the solid acid catalyst derived from Pongamia pinnata seed cake is compared with existing commercial catalysts. Thereby, the study encapsulates a comprehensive knowledge as application of lignocellulosic waste in the exploitation of catalysis.

2. Experimental

2.1. Materials

Pongamia pinnata seed cake was collected from nearby area of CSIR-IICT. Conc. H_2SO_4 of 98% purity was procured from Molychem, India. NaOH pellets (96.0% purity) and n-Butanol (99.0% purity) were purchased from Finar, India. Lactic Acid and Phenolphthalein indicator (PH 8.2–9.8) were procured from SRL and SD fine chemicals, India, respectively. Lactic acid with 30% strength was prepared by dilution of stock solution with distilled water for the esterification reaction.

2.2. Preparation of solid acid catalyst

The De-oiled Pongamia pinnata seed cake was obtained after expelling the oil. The approximate extractive content in the seed cake was found to be 40 wt % per 100 g of seed cake [18]. The cake was washed and the excess moisture content was reduced to $< 12\%$ by air drying for 1–2 day. The dried seed cake (SC) was then grinded using mortar and pestle and sieved to obtain uniform particle size. The seed cake was carbonized in clay pots sealed with m-seal using muffle furnace at 590 °C for 2 h with a heating rate of 10 °C/min under inert atmosphere of N_2 gas flow rate of 60 mL/min. The carbonized seed cake (CSC) was followed by the sulfonation process, which was carried out in a glass jacketed reactor. 10 g of CSC was treated with 200 ml of conc. H_2SO_4 (98%) solution, heated at 200 °C for 8 h. Thereafter the sulfonated carbonized seed cake was washed with hot distilled water to remove the unbound H_2SO_4. The sulfonated carbonaceous solid is dried at 100 °C under vacuum for 5 h to remove moisture and used as catalyst for esterification reaction [22].

2.3. Lignocellulosic sample characterization

The elemental (CHNSO) analyzer (Model: Elementar Vario micro cube, made in Germany) was used to quantify the carbon, hydrogen, nitrogen, sulphur, and oxygen percentage. Fourier Transform Infrared Radiation (FTIR) spectra of the samples were recorded using thin films of the samples placed between KBr discs. A total of 40 scans were needed to get a better signal-to-noise ratio. The spectra were recorded at $4\,cm^{-1}$ resolution in the range of $400–4000\,cm^{-1}$ on a Thermo Nicolet Nexus 670 Spectrometer. Scanning electron microscope (SEM) images of was taken using scanning electron microscope (Hitachi S-3000N) having an acceleration voltage of 10Kv to determine the surface morphology. The Powder X-ray diffraction (XRD) analysis was performed using a XRD spectrometer (Bruker D8 Advanced) with Cu/K α-radiation at 40 kV and 130 mA. The 2θ ranges were from 2.0° to 80.0° with the step of 0.05° for a step time of 0.5s with the scanning speed of 1°/min which collects the two-dimensional diffraction patterns of the sample. Thermogravimetric analysis (TGA)/differential thermal analysis (DTA) of samples was carried out using the Instrument TGA Q500 V20.13 Build 39 from Universal V4.5A TA Instruments. The sample weight was used around 1–5 mg for each analysis. The sample was placed n a platinum container and TGA was carried at a ramping rate of 10.00 °C/min with the sample gas as Nitrogen at a flow rate of 60.0 ml/min up to 800.0 °C. TGA has been used to obtain the optimum temperature for pyrolysis of feed stock. The thermogravimetric weight loss curve (TG, wt %) was recorded as a function of temperature. The thermal degradation depends on the amount of cellulose, hemicelluloses and lignin content of the sample. The Brunauer Emmett and Teller (BET) and N_2 adsorption-desorption isotherms analysis were performed to investigate the specific surface area and average pore size of samples using Instrument Quadra Sorb Station 2: version 5.06 with analysis gas as nitrogen at bath temperature 77.3 K for outgas time of 2.0 h and temp upto 150 °C.

2.4. Esterification reaction and optimization

The reaction was performed in Reactor Ready™ lab reactor from radleys of 500 mL capacity. The equipment was equipped with a Dean Stark leg, reflux condenser, digital overhead stirrer (direct controlled model with a motor rating of 83/75 W, maximum torque of 85 N cm and a speed range of 200–3000 rpm), a thermo well, a sampling port and PTFE stirring shafts impeller. The reactor has a provision for periodic withdrawal of liquid samples during the reaction. A WIKA digital thermometer (Model: CTH6200) was used for the measurement of reaction mixture temperature with an uncertainty of ± 0.1 K. The temperature of the reaction mixture was maintained by an automatic digital refrigerating and heating thermostat (Poly Science digital temperature controller).

In the experimental runs for the recovery of value added chemical, low strength lactic acid (30%) and the prepared catalyst were charged into the reactor and heated to desired temperature. The esterification was performed in a reactive distillation mode with continuous removal of water formed. At the onset of desired temperature, *n*-butanol added to the reactor, and this time was considered as the zero reaction time. An appropriate stirring speed of 250 rpm was maintained, which was