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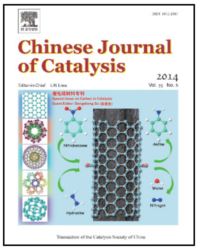

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Esterification of levulinic acid into ethyl levulinate catalysed by sulfonated hydrothermal carbons

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ABSTRACT

The synthesis of carbon-based, heterogeneous sulphonic catalysts for the production of levulinate esters. Hydrothermal treatment at moderated temperatures was employed to generate highly functional carbonaceous materials, referred to as hydrothermal carbons (HTCs), from both glucose, cellulose and rye straw. The products were sulfonated to generate solid acid-catalysts. Characterisation of the as-synthesised materials as well as catalyst activity tests were performed. SEM images indicate the micrometre-sized particles present in both HTCs were largely unaffected by sulfonation, although cellulose-derived HTC displayed signs of inadequate hydrolysis. FT-IR spectroscopy and elemental analysis confirmed successful incorporation of sulphonic groups. ^{13}C solid state NMR, in addition to TGA, elucidated the carbons' structural composition and supported the commonly-proposed hydrothermal carbonisation mechanism. Finally, the catalysts were tested via levulinic acid-ethanol esterification and gave high conversion and ester-selectivities (> 90%).

1. Introduction

Homogeneous-acid catalysts, such as sulphuric acid, have been recently used to produce biodiesel fuels. Although the homogeneous esterification of acids has been reported to give better conversion compared to heterogeneous esterification system, it is well-known that the use of mineral acids has some significant disadvantages associated with the handling, equipment corrosion due to their miscibility with the reaction medium, separation problems, disposal and regeneration due to their toxic and corrosive nature. The genesis of the green chemistry principles and increasing concerns about environmental issues, have stimulated the research for recyclable strong solid acids to replace of conventional toxic and corrosive acid catalysts [1].

Levulinate esters including ethyl, methyl, or butyl levulinate are the esterification products of levulinic acid and they have numerous potential applications in the flavouring and fragrance industry or as a blending component in biodiesel [2–4]. Biodiesel fuel has many favourable properties as a possible renewable extender for petroleum diesel fuel [2]. In addition to its renewability, other advantages of biodiesel include biodegradability, miscibility with petroleum diesel, increased lubricity, high flash point, and reduced emissions of particulate matter, unburned hydrocarbons, and CO during fully warmed-up conditions [3]. On the other hand, some of the known problems with biodiesel fuel include thermal and oxidative instability, poor low temperature flow properties (higher cloud point), increase in NO_x emissions, increased fuel consumption due to lower net heat of combustion, and increased unburned fuel and CO emission [4]. Levulinate esters are suitable as additives to biodiesel transportation fuels with excellent properties, such as

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low toxicity, high lubricity, flashpoint stability, and moderate flow properties under low temperature conditions [5].

The most applied method for the reaction of levulinic acid (LA) with alcohols to produce esters is in the presence of a homogeneous mineral acid or a heterogeneous catalyst. The esterification reaction can proceed in the presence but also in the absence of a catalyst. Uncatalysed reactions have been reported as a possible way for esters production, but the reaction rate is very slow, depending on the catalysis of carboxylic acid itself [6]. Bankole et al. [6] reported the uncatalysed esterification of various acids including levulinic acid to ethyl levulinate (levulinic acid:ethanol 1:1) at 25–250 °C. The highest conversion was achieved at 250 °C after 60 min (60% levulinic acid conversion), whereas the equilibrium was only 21% at 60 °C after 120 h reaction time. Levulinate esters were mainly produced from LA in the presence of mineral acids, which lead to a high yield of corresponding products [7–9].

Dharne et al. [10] studied esterification of levulinic acid to *n*-butyl levulinate over a heteropolyacid supported on acid-treated clay. An optimized *n*-butyl levulinate yield of 97% was achieved by using a catalyst of 20% dodecatungestophosphoric acid (DTPA) supported on K10. Methyl and ethyl levulinate were also synthesised in the presence of Keggin Unit-SiO_2 [11] catalysts, achieving a methyl levulinate yield of 73% and an ethyl levulinate yield of 68%. Silica-included Wells–Dawson heteropolyacid catalysts were explored for the synthesis of ethyl levulinate, analysis of the catalyst recycling experiments revealed that the 40WD-S catalyst exhibited excellent catalytic activity, although the product yield declined from 72% to 68% during three reaction cycles [12].

Sulfonated carbonaceous materials have been synthesized and investigated as environmentally benign, cheap, and recyclable catalysts for the production of biodiesel via the esterification of fatty acids. Budarin et al. [13] synthesized a sulfonated Starbon 400 with 0.5 mmol/g SO_3H loading. Sulfonated glucose microspheres (2–3 mm) were also synthesized (sulfur 0.57 mmol/g) by Fuertes et al. [14] and have been used for the esterification of oleic acid into of ethyl oleate. Wang et al. [15] also synthesized glucose-based catalysts by using *p*-toluenesulfonic acid as sulfur reagent, for the esterification of succinic acid with ethanol. The sulfur content of these materials was measured at 1.27 mmol/g.

However, to the best of our knowledge, biomass-derived carbon materials have not been yet employed as heterogeneous catalysts for the esterification of levulinic acid to levulinate esters. Especially important are in this respect the hydrothermal carbon (HTC) materials as they are prepared from biomass precursors under mild conditions (180–280 °C) [16]. Due to these mild reaction conditions they have hydrophilic surfaces with oxygenated surface groups such as –OH or –COOH. These groups already confer them an acidic character but it also allows their further modification with other functionalities [17]. Our group has already demonstrated the great potential of HTC materials as heterogeneous catalysts for various reactions where the hydrophilic character and the polar groups of these materials play a very important role [18]. Here we demonstrate for the first time the potential of sulfonated HTC materials to act as efficient heterogeneous acid catalysts for the conversion of levulinic acid into ethyl levulinate.

This is a proof of concept study where we have used commercially available levulinic acid. However, during the hydrothermal carbonization of various biomass precursors, important amounts of levulinic acid are detected in the liquid phase. The amount depends on the reaction conditions (i.e. precursor concentration, catalysts, temperature, time, etc.). Therefore, in the future we would like to use the biomass-derived HTC materials as heterogeneous catalysts for converting the "in situ" formed levulinic acid in the liquid phase in other important chemicals such as ethyl levulinates but also others.

2. Experimental

2.1. *Synthesis*

2.1.1. *Synthesis of HTC Carbons*

Various concentrations of biomass precursors (i.e. glucose, cellulose, rye straw) are added to 30 mL stainless steel autoclaves equipped with a Teflon inlet with or without HCl as catalyst. The autoclaves are then heated in an oven at 230 °C for 24 h. After the hydrothermal reaction, the samples (solid + liquid) are removed from the autoclave and centrifuged at a speed of 1400 rpm in order to separate the liquid from the solid phase. The solid phase is washed with ethanol and dried in a vacuum oven at 80 °C for 48 h prior to further characterisation and further use. The remaining liquid phase is filtered and stored in the fridge until further analysis. For the production of sulfonated HTC carbons, only the no acid catalysts (no HCl)-produced HTC materials will be used.

2.1.2. *Synthesis of HTC-S Carbons*

The as-produced HTC materials are treated with sulphuric acid. The purpose of this step is to functionalise these materials with –SO_3H groups and increase their acidity. The HTC materials are suspended in H_2SO_4 (99.999% purity, 10 mL acid per g of HTC material) and heated for 4 h at 80 °C [14]. After sulfonation, the solid materials are gently stirred overnight in 500 mL of water to remove all the unreacted sulphuric acid. Then, they are washed with distilled water until the pH of the supernatant is close to 7, and finally with ethanol. The materials are dried in a vacuum oven overnight at 60 °C, before being characterised and tested as catalysts in the esterification reactions. From now on, the sulfonated material will be referred as HTC-Precursor-S (e.g. HTC-Cell-S for cellulose, HTC-Glu-S for glucose and HTC-RS-S for rye straw).

2.2. *Characterisation*

Elemental composition was determined using a Vario El elemental analyzer. Scanning electron microscopy (SEM) was carried out on a FEI Quanta 3D Environmental SEM (ESEM) to observe the surface morphology of all samples. The samples were mounted on aluminium stubs and coated with gold prior to analysis.

For an initial detection of successful sulphonation and iden-