



Synthesis of ethyl levulinate as fuel additives using heterogeneous solid superacidic catalysts: Efficacy and kinetic modeling



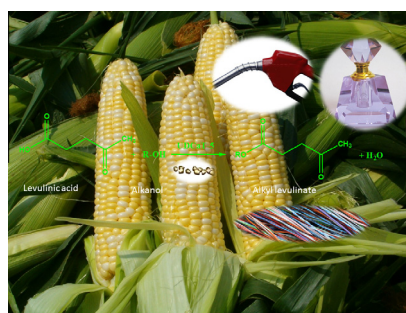
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HIGHLIGHTS

- Levulinic acid is an important bioresource for valorization.
- Modified sulphated zirconia catalyst UDCaT-5 most active and robust.
- Kinetics of ethyl levulinate synthesis as model process.
- Pseudo first order regime with energy of activation 9.00 kcal/mol.
- A variety of alkyl levulinates were synthesized using UDCaT-5.

GRAPHICAL ABSTRACT



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ABSTRACT

Esters of levulinic acid, which is biomass derived, are used as oxygenated additives in fuels, flavoring and fragrance industry or as blending components in biodiesel. A series of sulphated metal oxide catalysts were prepared and their activities were tested in the synthesis of ethyl levulinate as the model compound, among which UDCaT-5 (mesoporous super acidic zirconia modified catalyst) was the most active and robust catalyst. The effects of various parameters were studied in a batch reactor to establish kinetics and mechanism of reaction under optimized conditions. The reaction follows Langmuir–Hinshelwood–Hougen–Watson mechanism involving weak adsorption of the reactants and products. The apparent energy of activation was found to be 9.00 kcal/mol for ethyl levulinate. Several other alkyl levulinates were produced from esterification of levulinic acid with different alcohols using UDCaT-5. The use of solid acid catalyst made the process environmentally benign. The catalyst was reused up to four runs including the fresh one. A green and effective route for conversion of biobased levulinic acid into valuable esters is established.

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1. Introduction

Production of a variety of chemicals and oxygenated fuels from biomass is a tough task since biomass needs to be defunctionalized selectively using catalytic processes [1–4]. Both chemical and biological catalysts are being pursued worldwide to convert biomass into chemicals and biofuels [1–4]. The lignocellulosic biomass is a

potential alternative to non-renewable fossil fuels to meet future energy demands [1–3,5–9]. Biomass as feedstock is perceived to lessen CO₂ content in the atmosphere [10]. Particularly esters are important derivatives which can be prepared using heterogeneous catalysis [11,12] including renewable feedstock based esters as oxygenated fuels. Manufacture of levulinate esters, which are excellent renewable fuel additives, from cellulose, glucose and sucrose under acid catalysis using anhydrous conditions is highly desirable [13]. Biomass derived levulinic acid is considered as one of the top twelve building blocks to produce a spectrum of fuel additives, and as a precursor for polymer and resins [14,15]. A few reviews have appeared on commercial applications of levulinic

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Nomenclature

A	reactant species A, levulinic acid	k_{R2}	reaction rate constant, $\text{cm}^6 \text{mol}^{-1} \text{s}^{-1} \text{g-cat}^{-1}$
B	reactant species B, ethanol	w	catalyst loading, g/cm^3 of the liquid volume
AS	chemisorbed levulinic acid	X_A	fractional conversion of A
BS	chemisorbed ethanol	$-r_A$	rate of surface reaction, $\text{mol cm}^{-3} \text{s}^{-1}$
C	product species C, ethyl levulinate	k_1	pseudo-first order rate constant, s^{-1}
D	product species D, water		
S	vacant site		
C_A	concentration of A, mol/cm^3		
C_{A0}	initial concentration of A in bulk liquid phase, mol/cm^3		
C_{AS}	concentration of A at catalyst surface, mol/cm^3		
C_B	concentration of B, mol/cm^3		
C_{B0}	initial concentration of B in bulk liquid phase, mol/cm^3		
C_{BS}	concentration of B at solid surface, mol/g-cat		
C_C	concentration of C, mol/cm^3		
C_{CS}	concentration of C at solid surface, mol/g-cat		
C_S	concentration of vacant sites, mol/g-cat		
C_T	total concentration of sites, mol/g-cat		
			<i>Abbreviations for catalysts</i>
			S-ZrO ₂ sulphated zirconia
			S-SnO ₂ sulphated tin
			S-TiO ₂ sulphated titania
			FRSZ fuel rich sulphated zirconia
			UDCaT-5 University Department of Chemical Technology catalyst-5
			MUICaT-5 Mumbai University Institute of Chemical Technology catalyst-5
			UDCaT-6 University Department of Chemical Technology catalyst-6

acid and its derivatives [16,17]. Esters of levulinic acid find applications in perfume and flavor industry, as blending agents in biodiesel, as plasticizers, solvents, etc. [18]. 2-Methyl-tetrahydrofuran, a levulinic acid derivative, can also be employed as additive in diesel and gasoline. Amination of levulinic acid leads to δ -aminolevulinic acid is used as herbicide and the bisphenol derivative of levulinic acid is a good substitute for bisphenol A [19]. Ethyl levulinate is used on large scale as oxygenated additive in fuels among all esters of levulinic acid. Esterification of levulinic acid is usually carried out in liquid phase by using polluting mineral acids such as sulfuric, hydrochloric or phosphoric acids which ought to be converted into green processes using solid acids and superacids [20–22]. The superior properties of heterogeneous solid acids and superacids in developing green processes are well documented. Direct conversion of glucose into ethyl levulinate over sulphated metal oxides as catalysts at 200 °C is reported [23]. Keggin type and Wells–Dawson type of heteropoly acids as esterification catalysts are well known [24,25]. Although several new Lewis as well as Bronsted solid acid catalysts have been employed to get better yield, many of them still are beset with common disadvantages such as harsh conditions and poor reusability. With increasing emphasis on green chemistry and technology, efforts have been made to develop environmentally friendly and yet cost effective processes for esterification reactions. In recent decades, a great deal of attention has been focused towards use of sulfated zirconia (S-ZrO₂) based catalysts [26]. The activity and selectivity of different solid acids such as sulphated zirconia and UDCaTs [27–33], combustion synthesized FRSZ [34] and MUICaT series of super acidic catalysts [35] have been evaluated in green acylation, rearrangement and esterifications (see Supporting information).

The present work demonstrates the efficacy of a novel superacidic solid acid catalyst UDCaT-5 in esterification of levulinic acid to alkyl levulinates. A comprehensive investigation of various parameters was accomplished for ethyl levulinate and a kinetic model developed and validated against experimental results. The studies were extended to other esters.

2. Materials and methods

2.1. Chemicals

The following analytical grade reagents were procured from well-known companies and used as such. Zirconium oxychloride, tin chloride, titanium isopropoxide, aqueous ammonia solution,

chlorosulphonic acid, levulinic acid and ethanol were purchased from s.d. Fine Chem. Ltd., Mumbai, India. Tetraethyl orthosilicate was obtained from Fluka Germany.

2.2. Preparation of catalysts

Catalysts such as UDCaT-5 [29], UDCaT-6 [30], FRSZ [34] and MUICaT-5 [35] were prepared by well established procedures by our laboratory. Sulphated SnO₂ (S-SnO₂) and sulfated TiO₂ (S-TiO₂) were prepared by hydrolysis in similar manner as before for S-zirconia from precursors SnCl₂·2H₂O and titanium isopropoxide, respectively [29]. The solid was dried and washed with deionized water until a neutral filtrate with no chloride was obtained. Sulphation was carried out with 15 cm³/g of 0.5 M chlorosulphonic acid in ethylene dichloride for both Sn(OH)₂ and Ti(OH)₄ respectively, and calcined at 650 °C for 3 h [29].

2.3. Experimental set up

A stainless steel Parr autoclave (100 mL capacity) having a four blade-pitched turbine impeller was used as reactor. The temperature was controlled within ± 1 °C of the set value by PID controller. Predetermined amounts of reactants and the catalyst were charged into the autoclave and the temperature raised to the set value. It needed 20 min to get the set temperature of 160 °C until when the reaction mass was not agitated. Once the temperature was attained, a zero hour sample was withdrawn and sampling was done periodically. The control experiment was: 0.0375 mol levulinic acid, 0.75 mol ethanol, 0.01 g/cm³ catalyst loading, 160 °C, 1000 rpm.

2.4. Method of analysis of reaction mixture

Ethanol was taken in excess and the conversions were based on the limiting reactant, levulinic acid. Analysis of the reaction mixture was performed on GC (Chemito, model 1000) by using FID and a capillary wax column BPX-50 (0.22 mm diameter and 30 m length). The product was confirmed by GC–MS (Perkin Elmer instrument, Clarus 500) with BP-1 capillary column (0.25 mm i.d., 30 m length) and EI mode of MS. Synthetic mixtures were used for calibration and quantification of data. Figs. 1 and 2 show the FTIR and GC–MS of product i.e. ethyl levulinate respectively. The sharp peak at 1718.26 cm⁻¹ is for the ester of levulinic acid.

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