



One pot selective transformation of biomass derived chemicals towards alkyl levulinates over titanium exchanged heteropoly tungstate catalysts

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ABSTRACT

Alkyl levulinates were produced from biomass derived carbohydrates (glucose, fructose) and platform chemicals (5-hydroxy methyl furfural, furfuryl alcohol and levulinic acid) under feasible reaction condition using titanium modified heteropoly tungstate catalysts. Titanium exchanged heteropoly tungstophosphoric acid (TPA) with variation in titanium content were prepared and various spectroscopic methods were used to characterize these catalysts. The exchange of Ti in TPA essentially created new Lewis acidic sites. The existence of both Lewis and Bronsted acid sites of titanium containing TPA Keggin were directing the selective synthesis of alkyl levulinates from different starting materials. The partially exchanged $Ti_{0.75}$ TPA catalyst yielded about 92–98% of alkyl levulinates from 5-hydroxy methylfurfural, furfuryl alcohol and levulinic acid, whereas 63 and 21% yield was achieved by the alcoholysis of fructose and glucose respectively. Different types of alkyl levulinates were also synthesized from alcoholysis of furfuryl alcohol. The reaction conditions were optimized to achieve maximum yield of alkyl levulinates. The catalyst was easily separated and reused without any loss in activity.

1. Introduction

The dwindling of fossil reserves and CO₂ emission problems encouraged many researchers to develop new technologies for the transformation of renewable resources to bio fuels and useful chemicals [1]. The US Energy Department and the European Union has individually fixed a goal to replace conventional transportation fuels with biomass based fuels [2,3]. Biomass derived carbohydrates are the most accessible renewable resources and possess a great prospective raw materials to produce fuels and bulk chemicals [4,5]. These carbohydrates can be further transformed to platform chemicals like 5-hydroxymethyl furfural (HMF), furfuryl alcohol (FAL), levulinic acid (LA) and its esters [6–8]. Among the biomass carbohydrate-derived chemicals, alkyl levulinates have received particular attention due to their oxygenate fuel additive characteristics [9]. Alkyl levulinates are used as fuel additives in transportation fuels due to its unique properties such as non-toxic nature, high lubricity, flashpoint stability and finer flow properties under cold conditions [10]. Among the alkyl levulinates, ethyl levulinate (EL) is a better fuel additive because of its high solubility in diesel range fuels containing higher aromatics [11]. Alkyl levulinates have widespread applications as solvents and plasticizing agents. Alkyl levulinates possess CO₂ absorption properties and useful as solvent for sequestration processes [12,13].

In general, industrially alkyl levulinates are obtained by acid

catalyzed esterification of levulinic acid with the corresponding alcohol [14]. However, levulinic acid is a high cost raw material for this purpose. As the carbohydrates are cheap and readily available from renewable resources, its conversion towards alkyl levulinates in the presence of alcohol is considered as more appropriate approach [15–17]. A number of techniques has been developed for the production of alkyl levulinates from wide range of sources such as cellulose, saccharides, chloromethyl furfural, and FAL [18–21]. Earlier researchers used strong and corrosive homogeneous acids such as HCl and H₂SO₄ as effective catalysts for the alkyl levulinates production from sugars and furfuryl alcohol [22]. In recent times, sulfonic acid functionalized carbon materials [23], sulfonic acid functionalized mesoporous silica materials [24], zeolites [25], porous alumina silicates [26], arylsulfonic acid functionalized hollow mesoporous carbon spheres [27], sulfonic acid functionalized ionic liquids [28], have been investigated for the production of alkyl levulinates. Recently commercially available AlCl₃ and Al₂(SO₄)₃ were used as catalyst for the synthesis of ethyl levulinate [29]. However these catalysts have issues like complexity in separation from reaction mixture, reusability and environmental concerns. In order to defeat these issues the use of environmentally benign heterogeneous catalyst is an ideal approach.

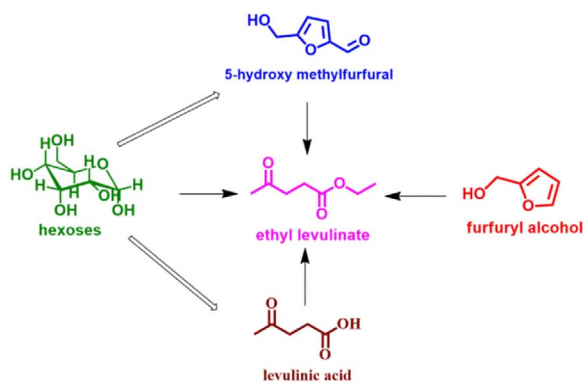
In recent years Keggin type heteropoly acids (HPAs) known for their strong Bronsted acidity has been used as catalysts for biomass conversion to important chemicals. The applications of HPA are limited since

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Scheme 1. Reaction pathways for the preparation of EL from biomass derivatives.

these HPAs are soluble in polar solvents. This can be overcome by modification in its primary or secondary structure. The substitution of protons of HPA with bulk cations like Ag^+ , Cs^+ , and Al^{3+} led to beat the solubility problem [30–34]. Modified HPA are not explored as suitable catalysts for the synthesis of alkyl levulinates. HPA-ZrO₂ based bifunctional catalysts and HPA supported on mesoporous silica were used for the preparation of alkyl levulinates from levulinic acid [35,36] and the overall activity is limited. There is a need to develop catalytic systems that can synthesis alkyl levulinates starting from carbohydrates.

In the current work, synthesis of alkyl levulinates from biomass derived carbohydrates (glucose, fructose) and its derived chemicals (5-HMF, LA, FAL) over titanium containing heteropoly tungstate catalysts was studied (Scheme 1). The catalytic activity was explained based on the characteristics derived from different spectroscopic techniques.

2. Experimental

2.1. Catalyst preparation

The chemicals $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, 12-tungstophosphoric acid (TPA) were received from Sigma–Aldrich chemicals and used as received. Ti-exchanged TPA ($\text{Ti}_{x/4}\text{H}_{3-x}\text{TPA}$, x is the quantity of Ti atoms in $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $x = 1, 2, 3$) catalysts with various Ti contents were prepared [37]. In a usual procedure of $\text{Ti}_{0.75}\text{TPA}$ preparation, 1 mol of TPA was taken in distilled water. Afterwards 0.75 mol of titanium (IV) isopropoxide, dissolved in ethanol was mixed with the solution with continuous stirring. The solution was kept at 45 °C with stirring. The excess water/ethanol was dried up using rotavapour and the desiccated catalyst masses were further dried overnight in an oven and calcined at 300 °C for 2 h. The other catalysts were also prepared in the same way as $\text{Ti}_{0.75}\text{TPA}$.

2.2. Catalyst characterization

DIGILAB Excalibur-IR spectrometer was used to record the FT-IR spectra via the KBr disc method.

The character of acidic sites of the catalysts was investigated by using pyridine adsorbed FT-IR spectroscopy in DRIFT mode at room temperature. In the typical experiment the degasification was done in vacuum at 200 °C for 3 h followed by suspending dry pyridine. Afterwards the overspill pyridine was evacuated by heating the catalyst sample at 120 °C.

Ultima-IV X-ray diffractometer of Rigaku Corporation, Japan was used to record the XRD spectra with 2° min⁻¹ scan speed in the scan range of 10–80° at 30 kV and 15 mA.

The nature of acidic strength and acidity of the catalysts were measured by temperature-programmed desorption (TPD) of ammonia. Ammonia TPD was carried on BELCAT-II (Belsorb, Japan) instrument.

In a standard experiment about 0.05 g sample was pre-treated in pure helium flow for 1 h at 300 °C. After the pre-treatment, the catalyst sample was soaked with He balanced 10% NH₃ gas for 1 h at 100 °C and He flushing was used to remove physisorbed ammonia at same temperature. Then the TPD profile was carried from 100 °C to 800 °C with the temperature raising rate of 10 °C min⁻¹ and the desorbed ammonia gas was measured.

Raman spectra were obtained with Horiba Jobin-Yvon LabRam HR spectrometer using He-Ne (Helium–Neon) laser source of excitation wavelength of 632.8 nm. About 10 mg of the powdered catalyst samples were kept on a glass plate below the microscope for measurements.

³¹P NMR spectra of solid samples were verified in a 400 MHz Bruker spectrometer. A 4.5 μs pulse was used with repetition time of 5 s between pulses in order to overcome saturation effects. Spinning rate was 5 kHz. All the measurements were taken by using 85% H₃PO₄ as standard reference at room temperature.

2.3. General reaction procedure

The experiments were conducted in a 15 mL sealed tube equipped with magnetic stir bar and was filled with bio-derived platform chemical (FAL, LA, HMF) (1 mmol), ethanol (4 mL) and catalyst (2.25 wt%) at 120 °C at varying reaction times from 30 min to 360 min. The Shimadzu 2010 gas chromatograph with a flame ionization detector was used to analyze the products by separating them on an INNOWax capillary column (diameter: 0.25 mm, length: 30 m). The products were further confirmed by GC–MS (Shimadzu, GCMS-QP2010S) analysis.

Alcoholysis of carbohydrate reactions were performed in a stainless steel auto clave charged with glucose/fructose (4 mmol), alkyl alcohol (16 mL) and catalyst (2.25 wt%) at 120 °C for a period up to 360 min. After the reaction, the cooled solution was shifted into a volumetric flask and diluted with distilled water. The solution was shaken well to settle the insoluble precipitates (humin) and the catalyst at bottom, and the upper liquid was filtered through 0.2 μm Nylon syringe filters. Then the samples were analyzed by HITACHI-HPLC system maintained at 50 °C with binary (2130) pumps, refractive index detector (2490). Sugar SC1011 (300 mm × 8 mm) column was used to separate the products with water flow at 0.8 mL/min. The products were calibrated by injecting known concentrations.

3. Results and discussion

3.1. Catalyst characterizations

Fig. 1 indicates the FT-IR spectra of $\text{Ti}_{x/4}\text{H}_{3-x}\text{TPA}$ catalysts along with TPA. The Keggin HPAs IR bands appeared in the region of 1100–700 cm⁻¹ [38]. All the catalysts exhibited the bands in the same region as that of bulk TPA. The peaks observed at 1082 cm⁻¹ was ascribed to vibrations of P–O_a (O_a – an oxygen atom bound to three W atoms and to P), 988 cm⁻¹ was responsible for the W=O_t (O_t – terminal oxygen), 890 cm⁻¹ was a W–O_c–W (O_c – a corner sharing bridging oxygen atom), and a responsible peak at 792 cm⁻¹ is related to W–O_e–W (O_e – an edge-sharing bridging oxygen atom). These results authenticating the Keggin ion structure was retained even after the protons of TPA exchanged with Ti.

The powder XRD patterns of the catalysts along with parent TPA were presented in Fig. 2a. All the catalysts showed three major reflections at 2θ of 10.28°, 25.51°, and 34.39° related to the crystalline structure of heteropoly Keggin ion. The $\text{Ti}_{x/4}\text{H}_{3-x}\text{TPA}$ catalysts exhibited a marginal shift towards higher 2θ values compared to bulk TPA as displayed in Fig. 2b. This shift is specifically observed at a 2θ value of 25.5° for the catalysts with increasing Ti content in the secondary structure of TPA. The shift to higher 2θ values compared to parent TPA is due to the contracted unit cell [39,40]. These results indicating the

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