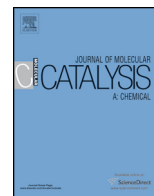




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Selective conversion of furfuryl alcohol into butyl levulinate over zinc exchanged heteropoly tungstate supported on niobia catalysts

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ABSTRACT

Selective synthesis of butyl levulinate by alcoholysis of furfuryl alcohol with *n*-butanol was achieved over of zinc exchanged tungstophosphoric acid supported on niobia catalysts. These catalysts were prepared and characterized by powder X-ray diffraction, FT-Infra red spectroscopy, pyridine adsorbed-FT-IR, temperature programmed desorption of ammonia, Laser Raman spectroscopy. The characterization results confirmed that the primary structure of Keggin ion of tungstophosphoric acid remained intact after exchange of its protons with zinc and subsequent dispersion on niobia. The exchange of Zn ions with the protons of heteropoly tungstate resulted in the creation of Lewis acidic sites. The catalysts were active for the synthesis of butyl levulinates under mild conditions within short reaction time. The activity of the catalysts related to the acidity of the catalysts which was dependent on the amount of Zn exchanged to the heteropoly tungstate on niobia. Reaction conditions were optimized and about 94% yield of *n*-butyl levulinate was achieved. The catalysts are reusable without any appreciable loss in activity.

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1. Introduction

The gradual decrease in fossil fuel resources and the impairment of environment led to look at alternative energy resources [1]. Cellulosic biomass is one of the abundant and renewable alternative energy resources [2,3]. Cellulose is the main source for the generation of sugars [4]. These sugars can be converted in to useful platform molecules such as 5-hydroxymethyl furfural, furfural and levulinic acid [5]. These platform chemicals can be further converted into commodity chemicals like furans, esters, polyols etc. Among the possible commodity chemicals alkyl levulinates are important chemicals due to their wide uses such as fuel additive, solvent, plasticizing and flavouring agents [6]. Alkyl levulinates are used in the synthesis of drug and chemical intermediates, since it contains both ketone and ester groups which makes them good building blocks [7]. Alkyl levulinates were identified in 2004 as one of the top ten biorefinery candidates. In particular, butyl levulinates is the food and drug administration of USA (FDA) approved flavour and fragrance. Butyl Levulinates were also used in solvent and plasticizer sectors [12]. Butyl levulinate is as one of the poten-

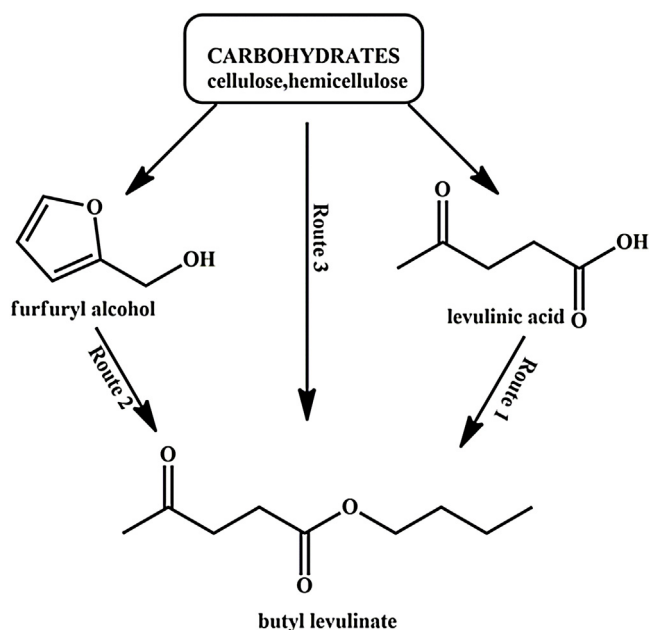
tial fuel additives with desirable characteristics among other alkyl levulinates.

There are three different routes for the preparation of alkyl levulinates from carbohydrates as shown in Scheme 1. The first route is the esterification of levulinic acid with alcohol in the presence of acid catalyst [8–11]. Secondly, furfuryl alcohol is also converted to alkyl levulinates by alcoholysis [12,13]. In addition to these two, there is a third route directly from carbohydrates [14,15]. Among these three routes preparation of alkyl levulinates from furfuryl alcohol is preferred due to its easy availability and high reactivity of alcoholysis reaction with desired selectivity compared to other methods.

The alcoholysis of furfuryl alcohol was carried using homogeneous and/or heterogeneous catalysts such as sulfonic acid-functionalized ionic liquids, sulfonic acid-functionalized carbon materials, zeolites, mixed-oxides, mesoporous alumino silicates, $\text{SO}_4^{2-}/\text{ZrO}_2$ and metal salts. Song and co-workers were investigated the production of alkyl levulinates from furfuryl alcohol in the presence of Bronsted acidic ionic liquids [16]. Chen et al. reported a series of sulfonic acid-functionalized carbon materials for dehydration of fructose to 5-hydroxymethylfurfural (HMF) and fructose alcoholises to alkyl levulinate [3]. Organo-inorganic hybrid solid acid catalysts were reported by Zhang et al. for the production of butyl levulinate with 93% yield from furfuryl alcohol. However, this catalyst was not reusable [7]. Valente and coworkers found that mesoporous alumino silicates (Al-TUD-1) were effective for

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Scheme 1. Possible reaction pathways for the preparation of butyl levulinate from biomass derivatives.

the production of useful bio-based levulinate esters from HMF or furfuryl alcohol with aliphatic alcohols [17,18]. Recently Peng et al. used commercially available AlCl_3 as a simple, cheap, and efficient catalyst for the synthesis of ethyl levulinate and the separation of the catalyst is difficult in this case [19].

Heteropolyacids (HPA) are well known as environmentally benign and economically feasible alternatives to traditional acid catalysts due to their Bronsted acidity, high proton mobility and relatively better stability. HPA exhibit excellent catalytic behaviour in a wide variety of acid-catalyzed reactions [20,21]. The disadvantages of heteropolyacids are due to their low specific surface area and high solubility in polar media. These demerits can be overcome by dispersing them on various porous materials and modifying them at their primary and secondary structure. Recently, the supported heteropolyacids have also been studied for the esterification of levulinic acid to produce alkyl levulinates [22]. Among the different possible acid and neutral supports to disperse HPA, niobia is well suited support. Niobia contains considerable amount of acidity which will be useful in obtaining highly acidic supported HPA catalysts.

Extension of our interest in development of modified Keggin type heteropoly acid catalysts for various acid catalysed transformations, in the present work, a series of niobia supported zinc exchanged tungstophosphoric acid (TPA) catalysts were prepared and studied for the synthesis of butyl levulinate (BL) from furfuryl alcohol (FAL) and butanol. The variation in acidity with the presence of Zn ions in TPA and its dispersion on niobia was studied and correlated with the activity of furfuryl alcohol alcoholysis.

2. Experimental

2.1. Catalyst preparation

The chemicals $\text{Zn}(\text{NO}_3)_2$, TPA procured from Sigma-Aldrich Chemicals and Nb_2O_5 was obtained from CBMM-Brazil and used as received. The catalysts were prepared in two steps. In the first step Zn exchanged TPA was prepared by ion exchange method [23]. The calculated amount of TPA (Sigma Aldrich Chemicals dissolved in amount of distilled water and required quantity of aqueous Zn

$(\text{NO}_3)_2$ solution was added drop wise with continuous stirring. The resulting mixture was aged for 1 h at 80°C . The excess water was evaporated to dryness on a hot plate. The obtained catalyst mass was oven dried at 120°C for 12 h and calcined at 300°C for 2 h. The catalysts were designed as Zn_xTPA where $x = 0.5, 1, 1.5$. In the second step, the required quantity of Zn_xTPA was dissolved in minimum amount of water and this solution was added drop wise to calculated amount of Nb_2O_5 with constant stirring. The excess water was removed by hot plate and the catalyst masses were dried in an oven at 120°C for 12 h. Finally the catalysts were calcined at 300°C for 2 h. These catalysts were denoted as $\text{Zn}_x\text{TPA}/\text{Nb}_2\text{O}_5$. The content of Zn_xTPA on niobia varied from 5 to 25 wt%.

2.2. Characterization of catalysts

FT-IR spectra of the catalysts were recorded on a DIGILAB (USA) IR spectrometer using the KBr disc method. The pyridine adsorption studies were carried out in the diffuse reflectance infra red Fourier transform (DRIFT) mode. In the typical experiment the catalyst was degassed under vacuum at 200°C for 3 h followed by suspending dry pyridine. Then, the excess pyridine was removed by heating the sample at 120°C for 1 h. After cooling the sample to room temperature, FT-IR spectra of the pyridine-adsorbed samples were recorded.

Powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a Rigaku Miniflex (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) with a scan speed of 2° min^{-1} and a scan range of $10\text{--}80^\circ$ at 30 kV and 15 mA.

Temperature programmed desorption of ammonia (TPD) was carried on BELCAT-II (Belsorb, Japan). In a typical experiment about 0.05 g of sample was pretreated at 300°C for 1 h by passing helium (99.9% , 30 mL min^{-1}). After pretreatment, the sample was saturated with anhydrous ammonia ($10\% \text{ NH}_3$ balance He) at 100°C for 1 h and subsequently flushed with He at the same temperature to remove physisorbed ammonia. Then the TPD analysis was carried out from ambient temperature to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ and the desorbed NH_3 was measured using thermal conductivity detector (TCD).

Confocal Micro-Raman spectra recorded at room temperature in the range of $200\text{--}1200 \text{ cm}^{-1}$ using Horiba Jobin-Yvon Lab Ram HR spectrometer with a 17 mW internal He-Ne (Helium-Neon) laser source of excitation wavelength of 632.8 nm. The catalyst samples in powder form (about 5–10 mg) were usually loosely spread onto a glass slide below the confocal microscope for Raman measurements.

2.3. General reaction procedure

All the reactions were performed in a 25 mL round-bottom flask equipped with magnetic stir bar. The reactants FAL (0.098 g, 1 mmol), *n*-butanol (6 mL) were taken in round-bottom flask and catalyst (0.3 g) was added to the reaction mixture. Then, the reaction was carried at 110°C for 5 h. The products were analysed by a gas chromatograph (Shimadzu 2010) equipped with a flame ionization detector using inno wax capillary column (diameter: 0.25 mm, length: 30 m). The products were also identified by GC-MS (Shimadzu, GCMS-QP2010S) analysis.

3. Results and discussion

3.1. Characterization

The FT-IR spectra of Zn exchanged tungstophosphoric acid catalysts along with Zn_1TPA and Nb_2O_5 are shown in Fig. 1. Niobia showed two intense broad bands centered around 695 and

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