

Lewis acidity induced heteropoly tungstate catalysts for the synthesis of 5-ethoxymethyl furfural from fructose and 5-hydroxymethylfurfural

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ABSTRACT

Heteropoly tungstate with tantalum ions in its secondary structure were prepared and subsequently dispersed on tin oxide. The prepared materials physical and chemical properties were estimated by different spectroscopic methods. Characterization results indicate that the stable Keggin ion of tantalum heteropoly tungstate was well preserved on support. New Lewis acidic sites were generated with the presence of Ta ions in heteropoly tungstate. These samples were tested for their catalytic performance towards conversion of fructose to 5-ethoxymethyl furfural (EMF) and selective etherification of 5-hydroxymethylfurfural (HMF) with ethanol. The catalyst with 30 wt% of active component on SnO₂ exhibited highest HMF etherification activity with 90% of 5-ethoxymethylfurfural yield with in 45 min. The catalysts also able to converted fructose into EMF in one-pot with a yield of 68%. The etherification activity over these catalysts was studied under the influence of different reaction parameters such as reaction temperature, reaction time, catalyst weight and reactants mole ratio.

1. Introduction

The world energy system is mostly dependent on the non renewable fossil fuel resources, particularly petroleum, coal and natural gas [1]. The gradual depletion of these energy sources, concerns regarding Green House Gases (GHG) emissions in the atmosphere and high demand for energy has become severe concern for researchers [2]. In order to overcome the problems of fossil fuels, researchers' attention was focused on finding alternative sustainable and eco-friendly energy sources [3]. Among the renewable resources, biomass is the only sustainable source to produce fuels, chemicals and carbon-based materials [4]. Biomass is broadly available in nature and different primary compounds like carbohydrates can be derived [5]. Carbohydrates are desirable resources for manufacture of bio fuels and valuable chemicals. Different methodologies have been explored to process abundant and cheaper biomass to chemicals/fuels [6].

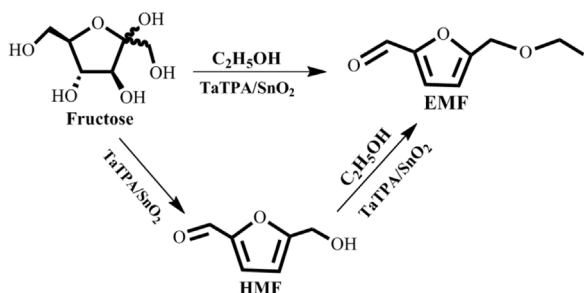
Production of different bulk chemicals is possible from biomass and among different chemicals 5-hydroxymethylfurfural (HMF) is considered as potential substitute for petroleum derived building blocks [7]. It is considered as a useful platform molecule to produce fine chemicals and fuel/fuel additives. HMF can be transformed to fine chemicals by hydrogenation, oxidation, esterification and etherification [8–10]. Among the wide range of possibilities, HMF etherification to 5-ethoxymethylfurfural (EMF) is important approach to synthesis fuel additives. EMF has energy density as diesel, high cetane number and in

certain cases it enhances the fuel properties [11,12]. In addition, EMF is able to convert to 5-ethoxymethylfurfuryl alcohol by hydrogenation. This hydrogenated product is more miscible with diesel and has analogous combustion properties as that of ethanol [13]. Therefore, EMF synthesis from renewable sources has gained considerable interest.

EMF can be prepared using different substrates like 5-chloromethylfurfural by nucleophilic substitution with ethanol [14], direct etherification of carbohydrates like fructose into EMF with alcohol in one-pot reaction as shown in Scheme 1. The etherification and direct conversion of fructose to EMF are acid catalyzed reactions. Therefore it is reasonable to carry fructose dehydration to HMF and its etherification into EMF in one-pot reaction. Etherification of HMF to EMF reaction was conceded using acidic catalysts like ionic liquids, organic-inorganic hybrid catalyst [15], H₃PW₁₂O₄₀ [16] and AlCl₃ [17]. The solubility of these catalysts in reaction mixture and/or polar solvents becomes difficult to separate the product from catalyst. In this contest there is a need to develop heterogeneous catalyst for one-pot conversion of fructose to EMF. Recently few researchers has studied heterogeneous catalysts such as MCM-41 supported HPW [18], silica coated magnetic Fe₃O₄ nano particles supported tungstophosphoric acid catalysts for both HMF and fructose etherification [19]. Recently Xiao fang Liu et al. used sulphated porous coordinated polymer (MIL 101- SO₃H) as a catalyst towards EMF synthesis from carbohydrates [20]. Lanza-fame and co-workers were used a mesoporous silica based catalysts for the translation of HMF to EMF [21]. Arenesulfonic acid-modified SBA-

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Scheme 1. Synthesis of EMF from fructose and HMF.

15 catalysts were tested for the conversion of fructose to EMF selectively [22]. Barbera et al. reported the conversion of HMF to EMF over zirconia and sulphated zirconia supported on SBA-15 catalysts [23]. Even though all of these catalysts reported high HMF conversion, requires lengthened reaction times. Moreover, these catalysts took long reaction time to yield reasonable amount of EMF when reaction carried from fructose.

Keggin type heteropolyacids (HPA) are commonly used as acid catalysts and these can be made heterogeneous by exchange of its protons (H⁺) with metal ions. These metal containing HPAs exhibit both Lewis and Brønsted acidic sites [24,25]. We have been working on metal exchanged HPAs for different acid catalyzed reactions [26,27]. In the current work, tungstophosphoric acid (TPA) was modified by exchanging its protons with Ta ion in order to generate Lewis acidity and dispersing the modified TPA on SnO₂ support. These catalysts were studied for the selective HMF etherification to EMF and also for one-pot conversion of fructose into EMF. The catalysts characteristics were derived from different techniques and used to explain the catalytic activity.

2. Experimental

2.1. Catalyst preparation

All the chemicals of AR grade were used in the study. Tantalum exchanged TPA (TaTPA) dispersed on tin oxide catalysts was prepared in two steps [28]. Firstly, TaTPA was prepared by the exchange protons of TPA with Ta ions. The calculated amount of TPA was completely dissolved in water and to this calculated amount of tantalum chloride (TaCl₅) dissolved aqueous solution of was added slowly with stirring. The resulting solution was stirred further for 1 h at 80 °C. The excess water was removed by rota evaporator to dryness. The samples were dried at 120 °C in an oven. Finally the catalyst samples were treated at 300 °C in air for 2 h.

Secondly, the prepared TaTPA was dispersed on SnO₂ by impregnation method. The measured quantity of TaTPA dissolved in water and slowly added to SnO₂. Similar procedure as described above was followed to obtain final catalysts. Catalysts with different TaTPA loading from 15 to 35 wt% were prepared. The catalysts are represented as x % TaTPA/SnO₂. Where x represents the weight percentage of TaTPA (x = 5, 10, 15, 20, 25, 30, 35).

2.2. Catalysts characterization

Rigaku Miniflex diffractometer was used to measure the X-ray diffraction patterns of the catalysts. Cu Kα radiation of 1.5406 Å at 40 kV and 30 mA and secondary graphite monochromatic was used to record the patterns. The measurements were carried in the 2θ range of 10–80°.

The BET surface areas were determined by using the N₂ physisorption-desorption studies at liquid N₂ temperature using BEL Sorb2 Instruments, Japan. Before analysis the samples were degassed at 200 °C for 2 h

The FT-IR spectra were measured using the KBr disc method on a

DIGILAB (USA) IR spectrometer. Pyridine adsorbed FT-IR spectroscopy was used to measure the nature of the acid sites (Brønsted and Lewis) of the catalysts. Diffuse reflectance infrared Fourier Transform (DRIFT) mode was adopted to record the spectra. Initially the catalyst surface was cleaned under vacuum at 200 °C for 3 h. Later dry pyridine was spread in to the sample and the physisorbed pyridine was driven off by heating the sample at 120 °C for 1 h. Pyridine-adsorbed spectra of samples was recorded after bring the sample to room temperature.

Horiba Jobin-Yvon Lab Ram HR spectrometer with a 17 mW internal He-Ne laser source with 632.8 nm of excitation wavelength was used. The powder samples of catalyst dispersed on a glass slide and the spectra was recorded by focusing at different position. The spectra were recorded in the range of 200–1200 cm⁻¹.

Temperature-programmed desorption of ammonia was carried out on BELCAT-II (Belsorb, Japan) instrument. About 0.05 g of oven-dried sample was taken and pretreated at 300 °C for 1 h by passing pure helium gas (99.9%, 30 mL/min). After pretreatment, the sample was saturated with anhydrous ammonia (10% NH₃-90% He mixture gas) at 100 °C for 1 h and was flushed with He gas at the same temperature to remove physisorbed ammonia. Then, the temperature programming was carried out from 100 to 800 °C with a temperature increment of 10 °C/min. The amount of NH₃ evolved was calculated using the calibrated thermal conductivity detector of the instrument.

The catalyst surface morphology of was observed by field emission scanning electron microscope (FE-SEM) of JEOL JSM-7610F equipped with an energy-dispersive X-ray spectroscopy. The sample powder was randomly deposited on carbon tape placed on a stub. Before imaging, the prepared sample was underwent gold metallization in order to improve picture resolution. FESEM pictures were taken at accelerating voltage of 2.00 kV with Secondary Electron Image probe (SEI) and the Gentle Beam (GB) mode.

Transmission electron microscope (TEM; Philips Tecnai FEI F20, operating at 200 kV) was used to observe the morphology and particle size of the catalysts.

2.3. Reaction of HMF to EMF and products analysis

HMF etherification was performed in a 15 mL sealed tube. In a usual procedure, HMF (0.126 g) was dissolved in ethanol (2 g) and 3.8 wt% of catalyst were taken in the tube. The reaction tube was kept in oil bath at desired temperature and stirred magnetically at 300 rpm. After completion of the reaction or desired time, the reactor tube was quickly removed from heating and the reaction mixture was cooled to room temperature. The sample was diluted by adding ethanol and subjected to centrifuge to separate the catalyst. The products were estimated by separating them on innowax capillary column of gas chromatograph (Shimadzu, 2010) equipped with flame ionization detector Products were also identified by GC-MS (Shimadzu, GCMS-QP2010S) analysis.

2.4. One-pot synthesis of EMF from fructose and products analysis

One-pot EMF synthesis from fructose was carried similarly as mentioned in the above Section 2.3. In this case 0.180 g of fructose, 6 mL of ethanol and 100 mg of catalyst were charged in to sealed tube. The products were analyzed by using HPLC system (HITACHI) with binary 2130 pumps, a manual sampler, and 2490 refractive index detector maintained at 50 °C. The products were separated in sugar column, maintained at 60 °C using water as mobile phase with a flow rate of 0.8 mL/min. Calibration was carried by using standard 5-HMF, fructose, EMF and EL solutions. The samples were diluted with a known volume of millipore water before analysis to prevent the over loading of the column. All the experiments were done in triplicates and reported within standard deviations of triplicates within 2.0%.

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