Contents lists available at ScienceDirect







journal homepage: www.elsevier.com/locate/mcat

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



P. Krishna Kumari, B. Srinivasa Rao, D. Padmakar, Nayeem Pasha, N. Lingaiah*

Catalysis Laboratory, Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Hyderabad, 500 007, Telangana, India

ARTICLE INFO

Keywords: 5-Hydroxymethylfurfural Fructose 5-Ethoxymethylfurfural Etherification Tungstophosphoric acid

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-ethoxy methyl furfural (EMF) and selective etherification of 5-hydroxymethylfurfural (HMF) with ethanol. The catalyst with 30 wt% of active component on SnO_2 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 5ethoxymethylfurfural (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], $H_3PW_{12}O_{40}$ [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]. Lanzafame and co-workers were used a mesoporous silica based catalysts for the translation of HMF to EMF [21]. Arenesulfonic acid-modified SBA-

E-mail address: nakkalingaiah@iict.res.in (N. Lingaiah).

https://doi.org/10.1016/j.mcat.2018.01.034

^{*} Corresponding author.

Received 21 August 2017; Received in revised form 26 December 2017; Accepted 29 January 2018 2468-8231/ © 2018 Elsevier B.V. All rights reserved.



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 K α radiation of 1.5406A° at 40 Kv and 30 mA and secondary graphite monochromatic was used to record the patterns. The measurements were carried in the 20 range of 10–80°.

The BET surface areas were determined by using the N_2 physisorption-desorption studies at liquid N_2 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 (Bronsted 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 physiosorbed 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%.



Fig. 1. XRD patterns of TaTPA/SnO₂ catalysts. (a) 5% TaTPA/SnO₂ (b) 10% TaTPA/SnO₂ (c) 15% TaTPA/SnO₂ (d) 20% TaTPA/SnO₂ (e) 25% TaTPA/SnO₂ (f) 30% TaTPA/SnO₂ (g) 35% TaTPA/SnO₂ (©) TPA (\bullet) SnO₂.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 displays X-ray diffractograms of the catalysts. The patterns related SnO₂ are predominant in all the catalysts. The diffraction lines at 20 values of 26.1, 33.5, 51.4, 54.4, 61.5, and 65.6 suggest the presence of tetragonal structure of SnO₂ [29,30]. The patterns related to Keggin ion of TaTPA were also observed at 20 value of 10, 25.2, 29.3 and 34.6 for the catalysts with above 20 wt% of TaTPA on SnO₂ [31]. The absence of Keggin ion characteristic patterns suggests the existence of TaTPA is highly dispersed on the surface. Crystalline phase of Keggin TaTPA are present when its content is \geq 20 wt% suggests the attainment of bulk nature of TaTPA on support.

Fig. 2 shows the Raman spectral patterns of the catalysts. The Raman spectrum of pure SnO_2 displayed primarily three bands at 474, 630 and 770 cm⁻¹. The existence of these bands in catalysts confirms the tetragonal structure of SnO_2 and this observation is in concurrence with XRD measurements [32]. In addition to these bands two more



Fig. 2. Raman spectra of TaTPA/SnO₂ catalysts. (a) 5% TaTPA/SnO₂ (b) 10% TaTPA/SnO₂ (c) 15% TaTPA/SnO₂ (d) 20% TaTPA/SnO₂ (e) 25% TaTPA/SnO₂ (f) 30% TaTPA/SnO₂ (g) 35% TaTPA/SnO₂.



Fig. 3. Pyridine adsorbed FT-IR spectra of TaTPA/SnO₂ catalysts. (a) 5% TaTPA/SnO₂ (b) 10% TaTPA/SnO₂ (c) 15% TaTPA/SnO₂ (d) 20% TaTPA/SnO₂ (e) 25% TaTPA/SnO₂ (f) 30% TaTPA/SnO₂ (g) 35% TaTPA/SnO₂.

bands at 1005 and 991 cm⁻¹ were observed, which were related to symmetric and asymmetric stretching vibrations of W = Ot of TPA Keggin structure. The bending mode of the bridging W–O–W bonds of the intact Keggin structure gives a Raman band at 220 cm⁻¹ and this band was noticed for the present samples also [33]. The Raman analysis indicate that with the increase in TaTPA loading on SnO₂, the band intensities related to SnO₂ were decreased and at the same time intense bands related to heteropoly acid were noticed. These results reveal that TaTPA Keggin ion was well preserved on the SnO₂ support. The Raman spectral information was in good conformity with the results made from FT-IR and powder XRD techniques.

FT-IR spectra of pyridine adsorbed TaTPA/SnO₂ catalysts are shown in Fig. 3. In generally TPA shows typical bands at 1485 and 1530 cm⁻¹ corresponding to Brønsted acid sites. TaTPA supported on SnO₂ catalysts displayed intense bands at 1445, 1480, 1530 and 1590 cm⁻¹. The bands at 1445 cm⁻¹ and 1580–1590 cm⁻¹ were assigned to pyridine adsorption on Lewis acidic sites and the band at 1485 cm⁻¹ is a combined band originating from pyridine bonded to both the Brønsted and Lewis acid sites [34,35]. The results point out that Lewis acid sites were generated after the replace of the protons of TPA with Ta metal ion.

The surface areas of the catalysts are presented in Table 1. The bulk SnO_2 and TaTPA has a surface area of 15 and $5 \text{ m}^2/\text{g}$ respectively. The

Table 1			
The physico-chemical	properties	of the catalysts.	

Catalyst	$S_{BET} (m^2/g)$	Acidity (mmol/g)
SnO ₂	15	0.064
TaTPA	5	1.351
5% TaTPA/SnO ₂	16	0.123
10% TaTPA/SnO ₂	17	0.134
15% TaTPA/SnO ₂	18	0.142
20% TaTPA/SnO ₂	23	0.344
25% TaTPA/SnO ₂	21	0.405
30% TaTPA/SnO ₂	19	0.415



Fig. 4. Temperature programmed desorption of NH₃ patterns of TaTPA/SnO₂ catalysts. (a) SnO_2 (b) 5% TaTPA/SnO_2 (c) 10% TaTPA/SnO_2 (d) 15% TaTPA/SnO_2 (e) 20% TaTPA/SnO₂ (f) 25% TaTPA/Sno₂ (g) 30% TaTPA/SnO₂ (h) 35% TaTPA/SnO₂ (i) TaTPA.

surface areas of the supported catalysts were increased after the dispersion of TaTPA on SnO₂ up to 20 wt% and thereafter a marginal decrease was noticed. The increase in surface might be related to the well dispersed TaTPA Keggin clusters on SnO₂.

TPD of ammonia was carried to know the acidic strength distribution and total acidity and the profiles of TaTPA/SnO2 catalysts are displayed in Fig. 4. The catalysts acidity calculated from TPD are tabulated in Table 1. Three types of desorption peaks in the range of 200-650 °C were observed. The catalysts with low content of TaTPA on support showed one desorption peak at 200 °C corresponds to weak acidic sites. Apart from this low temperature peak, a strong desorption peak in between 450 and 500 °C was also observed. This peak originated from the sites possessing moderate to strong acidity. As the TaTPA content increased a shift in the high temperature desorption peak to further high temperature. This guides us that the strong acidic sites were formed as the amount of TaTPA increased on support. Bulk TaTPA showed sharp desorption peak at 575 °C related to the sites of strong acidity. The total acidity of catalysts increased with incremental increase in TaTPA content from 5 to 30 wt% on support [36]. There was no much variation in acidity beyond 30 wt% TaTPA on the support.

Field emission scanning electron microscope pictures were displayed in Fig. 5. The images of 10, 20, 30, 35%TaTPA/SnO₂ catalysts were shown for the sake of clarity to observe the variation in the pictures. The SEM images of the catalysts reveal that the active component TaTPA was uniformly dispersed on SnO₂. The TaTPA clusters present on support were in below 100 nm size. At higher loading agglomerated TaTPA particles were seen particularly in the case of 35%TaTPA/SnO₂ catalyst.

Transition electron microscope images of the catalyst samples are presented in Fig. 6. TEM images of 20, 30, 35%TaTPA/SnO2 catalysts morphology was captured. The images indicate that the particle size of catalysts increased with increase in TaTPA content on SnO₂. The particle size was below 50 nm for the samples up to 30 wt% TaTPA/SnO₂. Further increase in TaTPA content to 35% the particle size was increased. The TEM images were in support of the morphology observed from FESEM.

3.2. Activity measurements

Molecular Catalysis 448 (2018) 108-115

etherification of HMF was evaluated and the results are presented in Table 2. The support SnO₂ showed about 2% conversion of HMF. Blank reaction was also performed and there was no conversion of HMF. Unsupported TaTPA was also tested and it gave near 100% conversion with 88.3% EMF yield. Although high HMF conversion and selectivity towards EMF was observed for TaTPA, it was partially dissolved in reaction mixture. In this regard, to make this catalyst heterogeneous TaTPA was supported on support SnO₂. The results suggest that with increase in TaTPA loading on SnO2 a substantial increase in HMF conversion and EMF yield was noticed. The HMF conversion was 35% with 30% EMF vield was observed for 5 wt% TaTPA/SnO₂ catalyst at 120 °C after 45 min. The catalysts with 30 wt% TaTPA on SnO₂ able to convert HMF completely with 90% EMF yield. NH₃-TPD results indicated the increase in acidity as the content of TaTPA increases on support and the 30 wt% TaTPA/SnO2 catalyst showed maximum acidity. The HMF etherification and EMF yields also followed the same trend as that of acidity profile of the catalysts. A linear correlation was observed between catalysts acidity and HMF etherification activity.

Bing Liu et al. reported high 92.9% EMF yield from HMF catalyzed by AlCl₃ which is not recyclable [17]. Silica supported SO₃H catalyst showed 83.8% of EMF yields from HMF at high reaction time of 10 h [37] and K-10 clay-HPW catalyst exhibited 91.5% of EMF yield after 10 h of reaction [38]. Although considerable EMF yields were reported, these catalysts took long reaction times. When compared with other catalytic systems, present catalyst 30 wt% TaTPA/SnO2 showed 90% of EMF yields with in 45 min. The efficiency of the TaTPA/SnO₂ towards HMF etherification with high EMF yields might be due to the presence of Lewis acidic sites which were generated with the exchange of Ta ions in TPA.

3.2.2. Effect of catalyst weight

As the 30 wt% TaTPA/SnO₂ catalyst showed better activity, further the reaction conditions were optimized on this catalyst. The catalyst weight influence on HMF etherification to EMF was studied and the outcome from this is shown in Fig. 7. The catalyst weight main influence was on the yield of EMF. A substantial increase in conversion of HMF was observed with incremental increase in catalyst weight from 1.9 to 7.6 wt% due to the available of more number of active sites. As the catalyst weight increased the yield of EMF also increased and about 90.2% EMF yield was obtained at a catalyst amount of 3.8 wt%. When the catalyst amount increased further to 7.6 wt% HMF conversion increased up to 100% but the yield for EMF was decreased to 87%. The decrease of EMF yield might be owed to the formation of ethyl levulinate (EL). The reason is that with increasing catalyst weight the availability of catalytically active sites also increased which also promote the further conversion of EMF into byproduct EL. The catalyst weight of 3.8 wt% is optimum for this reaction.

3.2.3. Effect of reaction temperature

The etherification of HMF was carried in the temperature range of 80-140 °C and the results projected in Fig. 8. HMF conversion was only 48.2% at 80 °C, and reached almost 100% conversion when the temperature increased up to 140 °C. The EMF yield also gradually increased from 44.2 to 90.2% with variation in temperature from 80 to 120 °C and marginally decreased to 82.8% at 140 °C. These results point out that EMF was not stable at high reaction temperatures and converted to EL. Our results were consistent with the results reported by Balakrishnan and co-workers [39]. Ethyl levulinate could be formed via two routes including direct ethanolysis of EMF and ring-opening hydrolysis of HMF followed by esterification. The formation of EL from EMF is evidenced as the formation of EL increased with reaction temperature. Thus, 120 °C is an appropriate reaction temperature for EMF formation selectively over TaTPA/SnO2 catalyst.

3.2.1. Etherification of HMF over TaTPA/SnO₂ catalysts

The catalytic performance of TaTPA/SnO2 catalysts for the

3.2.4. The role of reaction time

The consequence of reaction time on the HMF etherificaion to EMF



Fig. 5. FE-SEM images of (a) 10%TaTPA/SnO2 (b) 20%TaTPA/SnO2 (c) 30%TaTPA/SnO2 (d) 35%TaTPA/SnO2 catalysts.

was studied and the observations are depicted in Fig. 9. The conversion of HMF and EMF yield improved with increase in reaction time. The HMF conversion was only 53.7% with 42% EMF yield after 15 min of reaction time. As reaction time increased to 30 min both HMF conversion and EMF yield were increased. When the reaction time was 45 min the conversion of HMF reached to 99.5% with 90.2% EMF yield. Further increase in time over 45 min led to complete conversion and at the same time the yield of EMF decreased. This aspect is related to ethanolysis of product EMF to EL. Therefore, the optimal reaction time is 45 min for selective formation of EMF.

3.2.5. Effect of HMF to ethanol mole ratio

Effect of mole ratio of reactants on the etherification reaction was carried and the results are presented in Fig. 10. It is a key parameter to achieve high HMF conversion and EMF yield. The reaction was conceded with HMF to ethanol mole ratios ranging from 1:21 to 1:65. The conversion and yield increased with increase in the amount of ethanol. The maximum HMF conversion and EMF yield attained at a mole ratio of 1:43 and a marginal decreased in the conversion was observed above this ratio. The excessive amount of alcohol may dilute the reactant and blocking the active sites on the catalyst surface thereby decreasing the selective etherification of HMF. The EMF yield also decreased at higher ethanol concentrations due to the formation of other side products like DEF (5-(diethoxymethyl)-2-furanmethanol).

3.2.6. Reusability

The reusability of catalyst is an essential characteristic in the development of heterogeneous catalysts. After completion of the reaction, the catalyst was separated by centrifugation from the reaction mixture and washed with ethanol. Then, the recovered catalyst was dried in an oven at 80 °C for 2 h and used for next reaction cycle under the same conditions. As shown in Fig. 11, TaTPA/SnO₂ catalyst exhibited constant activity during reuse. Furthermore, the intrinsic heterogeneous

characteristic of TaTPA/SnO $_2$ catalyst can favor to recover the catalyst as well as the reaction products.

3.2.7. One-pot synthesis of EMF from fructose and ethanol

Although a high yield of EMF was obtained from HMF etherification, one-pot synthesis of EMF from fructose is a most attractive process, As the dehydration of fructose into HMF and the etherification of HMF into EMF both are acid-catalyzed reactions, it is rational to merge the two consecutive reactions into a one-pot reaction. Thus, EMF synthesis from fructose was carried and the results are shown in Fig. 12. It was noted that fructose conversion and EMF yield increased gradually as the reaction proceeded. The conversion of fructose was only 34% after 2 h with 20% EMF yield. As the reaction time increased to 4 h the fructose conversion reached to 65.6% with 41.5% EMF yield. Further enhancement in reaction time to 8 h the conversion of fructose reached to 100% with 68% of EMF yield. Comparison of EMF yields from fructose with that from HMF, the EMF yield from fructose was lower than that from HMF. The results reiterate that the dehydration of fructose into HMF might inversely promote the rehydration of HMF into levulinic acid and the alcoholysis of HMF into EL, which also lowered EMF yield. As the reaction time increased from 2 to 8 h, the yield of EL was also increased from 0.5 to 16.5%. The decrease in EMF yield was due to the formation of EL.

Comparing the results of earlier catalysts like Ar-SO₃H-SBA-15 [22], MCM-41 supported on TPA [18] and MIL-101-based sulfated porous coordination polymers [20] for one-pot synthesis of EMF from fructose with present catalyst, Ar-SO₃H-SBA-15 catalyst exhibited EMF yield of 63.4% at 116 °C with 8.3 vol.% of DMSO in 4 h of reaction time. However, the use of DMSO becomes difficult in separation of reaction products by conventional processes such as distillation, due to the sensitivity of EMF to high temperatures. MCM-41 supported on TPA catalysts reported 42.9% EMF yield in 24 h. MIL-101-based sulfated porous coordination polymers showed 67.7% of EMF yields at 130 °C







Fig. 6. TEM images of (a) 20%TaTPA/SnO₂ (b) 30%TaTPA/SnO₂ (c) 35%TaTPA/SnO₂ catalysts.

Table 2

Etherification of HMF to EMF over $TaTPA/SnO_2$ catalysts and their acidity values.

Catalyst	HMF conversion (%)	Yield (%)	
		EMF	EL
Without catalyst	0	0	0
SnO ₂	2.0	1.8	0
ТаТРА	100	88.3	11.7
5% TaTPA/SnO ₂	35.0	30	1
10% TaTPA/SnO ₂	52.5	46.4	2.5
15% TaTPA/SnO ₂	76.0	68	5.8
20% TaTPA/SnO2	83.0	76.1	5.9
25% TaTPA/SnO ₂	94.5	85.5	8.4
30% TaTPA/SnO2	99.5	90.2	9.0
35% TaTPA/SnO ₂	100	82	14.7

Reaction conditions: HMF (0.126 g), ethanol (2 g), catalyst weight (3.8 wt%), reaction temperature (120 $^\circ C)$, time (45 min).

after 15 h. However, these catalysts showed high EMF yields at long reaction times. While the present TaTPA/SnO₂ catalyst exhibited higher catalytic activity with 67.5% of EMF yield from fructose in ethanol at 120 °C within a reaction time of 8 h. The efficient activity of this catalyst compared to MCM-41 supported on TPA is due the presence of



Fig. 7. Effect of catalyst weight on etherification of HMF. Reaction conditions: HMF (0.126 g), Ethanol (2 g), Reaction temperature (120 $^\circ$ C), Time (45 min).





Fig. 8. Effect of reaction temperature on etherification of HMF.

 $\it Reaction\ conditions:$ HMF (0.126 g), Ethanol (2 g), Catalyst weight (3.8 wt%), Time (45 min).



Fig. 9. Influence of reaction time on etherification HMF.

 $Reaction\ conditions:$ HMF (0.126 g), Ethanol (2 g), Catalyst weight (3.8 wt%), Reaction temperature (120 °C).



Fig. 10. Effect of HMF to ethanol mole ratio on etherification of HMF. *Reaction conditions:* HMF (0.126 g), Catalyst weight (3.8 wt%), Reaction temperature (120 °C), Time (45 min).

Fig. 11. Reusability of TaTPA/SnO2 catalyst.

Reaction conditions: HMF (0.126 g), Ethanol (2 g), Catalyst weight (3.8 wt%), Reaction temperature (120 °C), Time (45 min).



Fig. 12. Activity profiles during one-pot synthesis of EMF from fructose over 30%TaTPA/ SnO₂ catalyst.

Reaction conditions: Fructose (0.180 g), Ethanol (6 mL), Catalyst weight (100 mg), Reaction temperature (120 °C).

Lewis acidic sites generated by the presence of Ta ions.

4. Conclusions

Ta exchanged TPA supported on SnO₂ catalysts was prepared with retention of Keggin ion structure of TaTPA. Lewis acidic sites were generated by the exchange of TPA protons with Ta ions. Etherification of HMF depends on the acid strength distribution and total acidity of the catalysts. The total acidity of the catalysts was related to the content of TaTPA on SnO₂. The optimum loading of TaTPA on SnO₂ was 30 wt% for obtaining high etherification activity with 90% EMF yield at 120 °C with in 45 min. This catalyst also showed high activity towards the one-pot synthesis of EMF from fructose with 68% yield at 120 °C with in 8 h. The catalyst was stable and showed consistent activity upon repeated use. The HMF etherification activity depended on reaction temperature, time, catalyst weight and HMF to ethyl alcohol mole ratio.

Acknowledgements

P. Krishna Kumari thanks to University Grants Commission (UGC), India for financial support in the form of Junior Research Fellowship. The authors thank Council of Scientific & Industrial Research (CSIR) for the financial support in form of Catalysis for Specialty Chemicals (CSC-0125) project under 12th Five Year Programme.

References

- A. Iriondo, A. Mendiguren, M.B. Güemez, J. Requies, J.F. Cambra, Catal. Today 294 (2016) 380–388.
- [2] L. Peng, L. Lin, J. Zhang, J. Shi, S. Liu, Appl. Catal A: Gen. 397 (2011) 259–265.
- [3] F. Yang, Z. Yuan, B. Liu, S. Chen, Z. Zhang, J. Ind. Eng. Chem. 38 (2016) 181–185.
 [4] K. Ghosh, R.A. Molla, Md. A. Iqubal, Sk. S. Islam, Sk. M. Islam, Appl. Catal. A: Gen.
- 520 (2016) 44–52.
- [5] R. Goyal, B. Sarkar, A. Bag, N. Siddiqui, D. Dumbre, N. Lucas, S. Bhargava, A. Bordoloi, J. Catal. 340 (2016) 248–260.
- [6] G. Raveendra, A. Rajasekhar, M. Srinivas, P.S.S. Prasad, N. Lingaiah, Appl. Catal. A: Gen. 520 (2016) 105–113.
- [7] B. Liu, C. Ba, M. Jin, Z. Zhang, Ind. Crops Prod. 76 (2015) 781-786.
- [8] A. Iriondo, A. Mendiguren, M.B. Güemez, J. Requies, J.F. Cambra, Catal. Today 279 (2017) 286–295.
- [9] B. Liu, Z. Zhang, K. Lv, K. Deng, H. Duan, Appl. Catal. A: Gen. 472 (2014) 64-71.
- [10] S. Albonetti, A. Lolli, V. Morandi, A. Migliori, C. Lucarelli, F. Cavani, Appl. Catal. B: Environ. 163 (2015) 520–530.
- [11] Y. Ren, B. Liu, Z. Zhang, J. Lin, J. Ind. Eng. Chem. 21 (2015) 1127–1131.
- [12] H. Li, K.S. Govind, R. Kotni, S. Shunmugavel, A. Riisager, S. Yang, Energy Convers. Manage. 88 (2014) 1245–1251.
- [13] E.J. Ras, S. Maisuls, P. Haesakkers, G.J. Gruter, G. Rothenberg, Adv. Synth. Catal. 351 (2009) 3175–3185.
- [14] M. Mascal, E.B. Nikitin, Angew. Chem. Int. Ed. 47 (2008) 7924–7926.
- [15] B. Liu, Z. Zhang, K. Deng, Ind. Eng. Chem. Res. 51 (2012) 15331-15336.
- [16] H. Wang, T. Deng, Y. Wang, Y. Qi, X. Hou, Y. Zhu, Bioresour. Technol. 136 (2013) 394–400.
- [17] B. Liu, Z. Zhang, K. Huang, Z. Fang, Fuel 113 (2013) 625-631.
- [18] A. Liu, Z. Zhang, Z.F. Fang, B. Liu, K. Huang, J. Ind. Eng. Chem. 20 (2014)

1977-1984.

- [19] S.G. Wang, Z.H. Zhang, B. Liu, J.L. Li, Catal. Sci. Technol. 3 (2013) 2104–2112.
- [20] X. Liu, H. Li, H. Pan, H. Zhang, S. Huang, K. Yang, W. Xue, S. Yang, J. Energy Chem. 25 (2016) 523–530.
- [21] P. Lanzafame, D.M. Temi, S. Perathoner, Catal. Today 175 (2011) 435-441.
- [22] G. Morales, M. Paniagua, J.A. Melero, J. Iglesias, Catal. Today 279 (2017) 305–316.
- [23] K. Barbera, P. Lanzafame, A. Pistone, S. Millesi, G. Malandrino, A. Gulino,
- S. Perathoner, G. Centi, J. Catal. 323 (2015) 19–32. [24] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171–198.
- [25] B.S. Rao, P.K. Kumari, D. Dhanalakshmi, N. Lingaiah, J. Mol. Catal. A: Chem. 427 (2017) 80–86.
- [26] G. Raveendra, M. Srinivas, P.S.S. Prasad, N. Lingaiah, Int. J. Adv. Eng. Sci. Appl. Math. 5 (2013) 232–238.
- [27] K.T.V. Rao, P.S.N. Rao, P.S.S. Prasad, N. Lingaiah, Catal. Commun. 10 (2009) 1394–1397.
- [28] Ch. R. Kumar, P.S.S. Prasad, N. Lingaiah, J. Mol. Catal. A: Chem. 350 (2011) 83–90.
 [29] J.A. Dias, E. Caliman, S.C.L. Dias, M. Paulo, A. Thyrso, C.P. de Souza, Catal. Today 85 (2003) 39–48.
- [30] Ch. R. Kumar, M. Srinivas, N. Lingaiah, Appl. Catal. A: Gen. 487 (2014) 165–171.
- [31] A.E.R.S. Khder, Appl. Catal. A: Gen. 343 (2008) 109–116.
- [32] B. Mallesham, P. Sudarsanam, G. Raju, B.M. Reddy, Green Chem. 15 (2013)
- 478–489.
- [33] K.T.V. Rao, B. Haribabu, P.S.S. Prasad, N. Lingaiah, Green Chem. 15 (2013) 837–846.
- [34] B.S. Rao, P.K. Kumari, D.D. Lakshmi, N. Lingaiah, Catal. Today (2017), http://dx. doi.org/10.1016/j.cattod.2017.05.040.
- [35] M. Srinivas, G. Raveendra, G. Parameswaram, P.S.S. Prasad, N. Lingaiah, J. Mol. Catal. A: Chem. 413 (2016) 7–14.
- [36] M. Mu, W. Fang, Y. Liu, L. Chen, Ind. Eng. Chem. Res. 54 (2015) 8893-8899.
- [37] B. Liu, Z. Zhang, RSC Adv. 3 (2013) 12313–12319.
- [38] A. Liu, B. Liu, Y. Wang, R. Ren, Z. Zhang, Fuel 117 (2014) 68–73.
- [39] M. Balakrishnan, E.R. Sacia, A.T. Bell, Green Chem. 14 (2012) 1626–1634.