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Utilization of renewable resources: Investigation on role of active sites in zeolite catalyst for transformation of furfuryl alcohol into alkyl levulinate

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ABSTRACT

A bio-derived furfuryl alcohol transformation into various high-value chemicals is a growing field of interest among researchers. This study reports an exclusive investigation of the porosity and active sites responsible for the efficient alcoholysis of furfuryl alcohol to alkyl levulinate by the aid of zeolite catalyst. Alkyl levulinate is a promising platform chemical potentially used as a fuel additive and also for the production of chemicals. A detailed study using well-characterized HZSM-5 catalyst on the influence of acidity and post synthesis modification like desilication, dealumination, metal ion exchange and phosphate modification revealed the most desired type of acid sites required to catalyze this reaction. Among the HZSM-5 catalysts tested, HZSM-5 (SAR 95) showed the best performance of \geq 99 % furfuryl alcohol conversion and 85 % butyl levulinate selectivity under optimum conditions. The catalyst exhibited good recyclability additionally addressing all the challenges reported in the previous literature fulfilling the green chemistry principles.

1. Introduction

The present era of globalization is leading to the exhaustion of the conventional fossil fuels which would diminish the chance of meeting the energy demands for the future. The impact of the oil on mankind and its disastrous effects such as an increase in oil price, carbon footprint, foreign oil dependency, and disturbing world peace is evident. Despite its applications in daily life, extraction by mining and drilling itself has a lot of detrimental effects on our ecosystem such as landslides, flash floods, water pollution and greenhouse gas emissions. Due to the decrease in the reserves of these non-renewable resources, there is a serious necessity to switch into renewable resources which are abundant, carbon-neutral and environmentally friendly. Apparently, as the oil well drains up, not only the production of transportation fuels is affected, but also the petrochemicals manufactured from crude oil and its derivatives. There are excellent alternatives for fuels and energy production which can replace fossil fuels, for instance, solar energy, wind energy, nuclear energy, biomass, etc. However, these resources chosen should also effectively compete with the existing technology to produce chemicals. Apart from fossil fuels, the only two sustainable, renewable carbon sources are biomass and CO2. Therefore, exploiting

biomass for manufacturing commodity chemicals, fuels and fuel additives has gained a lot of consideration in recent years. Among the various chemicals obtained from lignocellulosic biomass, such as., glycerol, lactic acid, serine, aspartic acid, threonine, sorbitol, levoglucosan, xylitol, arabinitol, etc., furfural is projected as one of the 30 potential candidates as building blocks that would transform into multiple functionality chemicals [1].

Furfuryl alcohol produced by chemoselective hydrogenation of furfural is an abundant, C-5 sustainable platform chemical used for the synthesis of high-value products like lysine, methyl furan, ascorbic acid, levulinate esters, angelica lactones, γ -valerolactone, lubricants, resins, plasticizers, fragrances and adhesives [2,3]. Annually 62 % of the globally produced furfural (approximately 200 000 tonnes) is consumed for the synthesis of furfuryl alcohol due to its expanding application profile and increasing market value. Alcoholysis of furfuryl alcohol yields alkyl levulinate (Scheme 1) that has potential applications as biofuels and, additives in flavor and fragrance products [4]. As alkyl levulinates are traditionally produced by the esterification of levulinic acid, an expensive chemical, alcoholysis of furfuryl alcohol serves as an inexpensive route which also promotes the bio-based economy. This reaction utilizing furfuryl alcohol is challenging as the intermediate

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2-(alkoxy methyl) furan (AMF), an ether, formed is to be successfully converted into alkyl levulinate (keto ester) which is difficult compared to carboxylic acid route (levulinic acid). Hence alcoholysis of furfuryl alcohol is a greener approach to yield alkyl levulinate which helps to understand and explore the reaction.

For the liquid phase butanolysis of furfuryl alcohol to butyl levulinate, various solid acid catalysts have been reported which includes, graphite oxide (GO) and reduced graphite oxide (rGO) catalysts [5], lignin-based carbonaceous acid [6] modified SBA-15 [7-9], titanium exchanged mesoporous silica [10], modified ionic liquids [11,12], ionic liquids [13], zinc exchanged heteropoly tungstate supported on niobia [14], hematite [15], functionalized fibrous silica, [16], sulfonic acid functionalized TiO₂ nanotubes [17], tin exchanged tungstophosphoric acid and tin phosphate [18,19]. From these reports, it is understood that the Brönsted acid site plays a major role in the selective synthesis of alkyl levulinate. However, many of these reported catalysts have not been studied reusability or failed to retain their catalytic activity upon recycling [5,9,12,13,15,17,6]. The catalyst deactivation is mainly because of the accumulation of oligomeric products formed due to the polymerization of furfuryl alcohol on the active sites of the catalyst. Hence, high thermal stability should be one of the important virtues of the desired catalyst for this reaction as the catalyst regeneration at high temperatures is easily achievable. Some catalysts also reportedly gave good catalytic performance only in the presence of excessive usage of catalyst or reactants. [7,10-12,14,15,17,18,19] One promising catalyst that can overcome all these drawbacks is zeolite owing to its high surface area, strong Brönsted acidity, ordered microporosity, high thermal stability and better recyclability.

There are a few reports, where zeolite based catalysts have been investigated for this transformation. Lange et al. explored a range of acid catalysts such as H₂SO₄, ion-exchanged resins and zeolites in a semibatch semi-continuous mode at varied temperatures (125 and 225 °C) for the ethanolysis of furfuryl alcohol. The ZSM-5 (SAR30) was reported to give 65 mol% ethyl levulinate yield which is the best among the other zeolites tested (ZSM-5, ZSM-12, ZSM-23, H-Beta, mordenite). However, zeolites as such were ranked low among the other catalysts [20]. In another study by Yao-Bing Huang et al., HZSM-5 and H-Beta catalysts were compared with various metal salt catalysts under microwave irradiation. The metal salt Al₂(SO₄)₂, showed 80 % yield for methyl levulinate, whereas HZSM-5 and H-Beta showed 4.9 and 1% yield respectively [21]. A study on zeolite-based material was reported over H-ZSM-5, hierarchical zeolite, H-Beta and USY for ethanolysis of furfuryl alcohol by Nandiwale et al. [22]. The trend for ethyl levulinate yield was 5%, 8%, 13 % and 19 % for USY, H-Beta, HZSM-5, hierarchical zeolite respectively. Under optimized reaction conditions, hierarchical zeolite was found to be the most active catalyst with ethyl levulinate yield of 73 %. Additionally, other literatures are focusing on various catalysts by comparing their catalytic performance with zeolites [8-10,12,16, 23-25].

From the careful literature survey, we found that zeolite, in general, can be a potential catalyst for alcoholysis of furfuryl alcohol, but a detailed study over the zeolite to explore its properties to achieve enhanced performance has not been conducted so far. Moreover, a thorough study on the zeolite catalyst for this reaction is important to understand the intricacies of how the structural and textural properties of the catalyst influence the catalytic reaction. Hence, in this work, a

series of conventional solid acid catalysts were tested which included ordered mesoporous aluminosilicate, ion-exchange resin, silicoaluminophosphate, medium and large pore zeolites. Zeolite ZSM-5 was studied in detail to understand the relation between its physicochemical properties and the alcoholysis reaction. To discover the desired type of acid site for this reaction, post-modification of ZSM-5 was performed by desilication, dealumination, phosphate modification and metal ion exchange. The physicochemical properties of all the catalysts were investigated using various characterizations such as XRF, PXRD, nitrogen adsorption-desorption isotherms, NH3-TPD and SEM. Reaction parameters such as catalyst concentration, reactants mole ratio and temperature were studied using the catalyst with the best performance. To evaluate the reusability of the potential catalyst, the material was screened for multiple cycles at the optimized reaction conditions.

2. Experimental section

2.1. Materials

ZSM-5 with different SiO₂ to Al₂O₃ ratio (SAR), mordenite (SAR20), H-Beta (SAR25), were obtained from Nankai University Catalyst Co. China. ZSM-5 (SAR22) and Y-Zeolite (SAR 5.1) were procured from Zeolyst International. Furfuryl alcohol, ammonium dihydrogen phosphate (NH₄H₂PO₄), copper nitrate trihydrate, zinc nitrate hexahydrate, tetraethyl orthosilicate, concentrated HCl, concentrated H2SO4, concentrated H₃PO₄, ammonium acetate, aqueous ammonium hydroxide, Al(NO₃)_{3.} NaOH, 1-butanol, 1-propanol and methanol were purchased from Merck India Pvt. Ltd. Amphiphilic triblock co-polymer poly-(ethylene glycol)-block poly-(propylene glycol)-block poly-(ethylene glycol), ludox, fumed silica and morpholine were purchased from Sigma-Aldrich. Tetrapropyl ammonium bromide, zirconium oxychloride octahydrate were purchased from Loba Chemie. Citric acid and ethanol were procured from Otto biochemical reagents and CSS respectively. Amberlyst-15 was obtained from Alfa-Aesar. Plural SB (pseudoboehmite) was procured from Sasol.

2.2. Catalyst synthesis

HZSM-5 catalyst was synthesized from the procedure similar to the reported one [26]. In a typical synthesis, the required quantity of NaOH, Al(NO₃)₃ (aluminium source), ludox (silicon source) were added to the distilled water and stirred well. To this, a template tetra propyl ammonium bromide was added. The solution was transferred to a teflon lined autoclave and placed in an oven for 24 h at 180 °C. The material is washed filtered, dried and calcined at 550 $^\circ\text{C}$. To obtain the ammonium form of the synthesized and commercially obtained ZSM-5, the material was subjected to three-fold ammonium exchange using 0.5 M ammonium acetate for 4 h at 80 °C. The material was finally calcined at 550 °C for 5 h at a heating rate of 5 $^\circ C\mbox{min}^{-1}$ to yield the protonic form of the material [27]. The obtained materials were labelled as HZSM-5.

Other catalysts such as sulfated zirconia, SAPO-34 and Al-SBA-15 were synthesized from the reported literature [28-30]. Post modification procedures such as desilication, dealumination, phosphate modification, metal ion exchange are provided in ESI Section 2.2.

For recyclability study, the spent catalyst was washed with methanol, filtered, dried and finally calcined at 550 °C for 5 h after each



Alkoxy methyl furan

Scheme 1. Conversion of furfuryl alcohol to alkyl levulinate.

catalyst recycle.

2.3. Catalyst characterization

To determine the silica to alumina ratio (SAR) quantitatively, the catalysts were analyzed using X-ray fluorescence spectroscopy with the consideration of loss on ignition (LOI) using S4 Pioneer sequential wavelength-dispersive X-ray spectrometer (Bruker).

PXRD patterns of all the catalysts were recorded using Bruker D2 phaser X-ray diffractometer with Cu K α radiation as a source and wavelength of radiation $\lambda = 1.542^{\circ}$ A with high-resolution Lynxeye detector. Diffraction patterns were recorded by scanning all the catalysts through the 2 θ range of 5–60° (step size of 0.02° s⁻¹).

Scanning electron microscope (SEM) micrographs of HZSM-5 were recorded using Hitachi SU instrument to explore the morphology and particle size of the catalysts.

The nitrogen adsorption-desorption isotherms were obtained using Belsorp-mini II instrument (Bel, Japan) at liquid nitrogen temperature (-196 °C). All the catalysts were degassed at 300 °C for 4 h prior to the analysis. The specific surface area of the catalysts was determined using the Brunauer-Emmett-Teller (BET) equation. The pore volume of the catalysts was obtained using the MP plot.

The acidity of the modified and parent HZSM-5 catalysts was analyzed using the Belcat II instrument (Bel, Japan) by employing temperature-programmed desorption. NH₃ was used as a probe molecule and the instrument was equipped with a thermal conductivity detector. All the catalysts were pretreated at 550 °C for 1 h with the carrier gas, helium and cooled to 50 °C. The materials are then saturated with ammonia/helium stream for 30 min and are purged with helium for 15 min to remove the physically adsorbed ammonia. The ammonia desorption was recorded with a temperature program ranging from 50 to 550 °C with a heating rate of 10 °C min⁻¹. The deconvoluted data for all the conventional catalysts, ZSM-5 with varied SARs and post modified ZSM-5 were obtained. The strength of acidity viz. weak, moderate and strong was calculated at temperatures, <200 °C, 200–350 °C and >350 °C respectively.

The Brönsted and Lewis acid sites for all the post modified ZSM-5 catalysts were investigated by the aid of pyridine adsorption experiments using FTIR instrument (Bruker Alpha-T). The catalyst in the form of the self-supported wafer was calcined at 550 °C and saturated with pyridine at room temperature. It was then heated at 150 °C for an hour to remove the physisorbed pyridine. The subtraction of the FTIR spectrum after pyridine adsorption with that of untreated catalyst in the wavenumber range of 1410 –1560 cm⁻¹ gives the peaks only due to pyridine–acid site interaction.

2.4. Catalytic activity studies

In a typical procedure, the alcoholysis of furfuryl alcohol was performed in a liquid phase batch reaction under magnetic stirring at the desired temperature. The required molar composition of furfuryl alcohol and butanol, and the catalyst (with respect to the total reactants) were taken in a 25 mL round bottom flask connected to a condenser. The reaction of furfuryl alcohol was also conducted with other alcohols with a similar procedure under reflux conditions. The samples of the reaction mixture were periodically collected and quantitatively analyzed by gas chromatography (GC) (Agilent Technologies 7820A) equipped with HP-5 capillary column (0.25 mm I.D., 30 m length) coupled with the flame ionization detector. The identity of the products was confirmed by Gas chromatography mass spectrometry (GCMS). The furfuryl alcohol conversion and butyl levulinate selectivity were determined using the external standard method in the GC.

$$X_{FA}(\%) = rac{C_{FA(i)} - C_{FA(f)}}{C_{FA(i)}} \times 100$$

$$S_{BL}(\%) = \frac{C_{BL}}{C_{FA(i)} - C_{FA(f)}} \times 100$$

Where X_{FA} and S_{BL} are furfuryl alcohol conversion and butyl levulinate selectivity respectively. $C_{FA(i)}$ and $C_{FA(f)}$ correspond to initial and final molar concentrations of furfuryl alcohol respectively. C_{BL} is the molar concentration of butyl levulinate formed in the reaction.

3. Results and discussion

3.1. Characterization of the catalysts

XRF analysis provided the silica to alumina ratio (SAR) of all the commercial and synthesized zeolite catalysts tested for this transformation. The ZSM-5 zeolites with a wide range of SAR from 22 to 160 were chosen for this study.

All the diffractograms of HZSM-5 with varied SARs reflect the characteristic pattern of MFI topology with main peaks at $20 \ 13^{\circ}$, 23° and 45° [ESI Fig. S1 (a)] [31]. XRD patterns after the modifications such as desilication, dealumination, phosphate modification and metal ion exchange showed no change in the structure [ESI Fig. S1 (b–e)]. Also, the XRD patterns of SAPO-34, sulfated zirconia, Al-SBA-15, mordenite, H-Beta, Y-zeolite matched well with the literature. [ESI Fig. S2 (a–f)].

SEM analysis of HZSM-5 (SAR95) was performed to investigate the morphology and the particle size. The micrographs disclosed that the material contained spherical morphology with an average particle size of 0.5 μ m (Fig. 1).

The BET surface area of unmodified HZSM-5 with varied SARs was around 400 m² g⁻¹ which confirms its high surface area (Table 1). The post-modification, by desilication, metal ion exchange, phosphate modification, led to the decrease in surface area as shown in the Table1. But in the case of dealumination, there was a negligible increase in surface area. Also, there was a marginal difference in pore volume among the catalysts. Sorption studies were performed for all the catalysts tested which showed comparable results with the literature (ESI Fig. S3, Fig. S4). [28–30]

The total acidity of HZSM-5 from NH₃-TPD decreased from 1.06 to 0.28 mmol g⁻¹ with an increase in SAR from 22 to 160 as expected [Fig. 2 (a), Table 1]. The strengths of acidity of all the unmodified HZSM-5 catalysts were dominated by weak and moderate acidic sites. Among them, SAR 57 and 95 possessed a good number of strong acidic sites. Sulfated zirconia and Al-SBA-15 possessed acid strength in the broad range of 50–550 °C. Y-zeolite contained a similar number of weak and moderate acid sites, whereas H-Beta possessed predominantly strong acid sites. SAPO-34 and Y-zeolite contained mainly weak and moderate acid sites. [Table 1, ESI Fig. S5 (b–g).]

The treatment of HZSM-5 with 0.1 M NaOH decreased the acidity drastically from 0.59 to 0.29 mmol g^{-1} which might be due to the removal of extra framework aluminium along with the desired silicon atoms. For 0.2 M NaOH treatment, the acidity of the catalyst decreased to 0.38 mmol g^{-1} but it was still higher than 0.1 M NaOH treated catalyst. It is because the efficiency of desilication increased with increase in molar concentration of NaOH to 0.2 M, thereby increasing the acidity by removing more silicon atoms compared to the 0.1 M NaOH. However, a subsequent increase in the concentration of NaOH treatment might remove more number of silicon atoms but at the expense of the framework stability. [32] Hence, the NaOH treatment was stopped to 0.2 M concentration. In both the treatments of NaOH, the structural integrity of HZSM-5 was found to be retained by PXRD indicating that the zeolite framework was still stable after the removal of silicon atoms. Upon desilication, the B/L ratio of HZSM-5 decreased from 3.9 to 2.1 and 2.0 for 0.1 M NaOH and 0.2 M NaOH treatment respectively (Table 1, ESI Fig. S6). This is due to the generation of extra framework aluminium and also reincorporation of leached Al species resulting in an increase in Lewis acidity.



Fig. 1. SEM images of HZSM-5 (SAR95).

Table 1			
Physicochemical	properties	of the	catalysts

Catalyst	Surface area $(m^2 g^{-1})^{[a]}$	Pore Volume (cm ^{3} g ^{-1})	Acidity (mmol g ⁻¹)	Acidity (mmol g ⁻¹) ^[b]			B/L ^[d]
			Weak	Moderate	Strong	Total	
Sulfated Zirconia	78.2	0.12	0.03	0.10	0.11	0.25	-
SAPO-34	666.6	0.28	0.89	0.55	0.24	1.69	_
Amberlyst-15	40.3	0.27	-	-	-	4.7 ^[c]	_
Al-SBA-15 (SAR35)	677.4	0.88	0.07	0.05	0.06	0.19	-
Y-Zeolite (SAR5.1)	809.5	0.36	0.67	0.66	0.26	1.6	_
H-Beta (SAR25)	592.1	0.16	0.20	0.28	0.43	0.92	_
Mordenite (SAR20)	498.0	0.21	0.63	0.22	0.48	1.34	_
HZSM-5 (SAR22)	403.7	0.17	0.53	0.13	0.39	1.06	-
HZSM-5 (SAR57)	422.1	0.18	0.29	0.10	0.42	0.82	-
HZSM-5 (SAR95)	418.9	0.19	0.19	0.18	0.21	0.59	3.9
HZSM-5 (SAR117)	404.6	0.18	0.20	0.08	0.16	0.45	-
HZSM-5 (SAR160)	426.9	0.19	0.10	0.03	0.14	0.28	_
DS (0.1 M NaOH)	364.6	0.18	0.12	0.07	0.09	0.29	2.1
DS (0.2 M NaOH)	404.8	0.18	0.16	0.10	0.12	0.38	2.0
DA (HCl)	423.5	0.19	0.05	0.10	0.07	0.24	1.9
DA (Citric acid)	421.8	0.19	0.18	0.17	0.18	0.53	4.6
1% P-ZSM-5	403.1	0.18	0.17	0.14	0.11	0.42	4.3
3% P-ZSM-5	373.4	0.17	0.18	0.12	0.10	0.40	6.8
5% P-ZSM-5	323.7	0.15	0.16	0.13	0.08	0.37	5.3
Cu-ZSM-5	411.6	0.18	0.11	0.18	0.16	0.45	0.8
Zn-ZSM-5	417.1	0.19	0.14	0.17	0.17	0.48	1.2

[a] BET surface area, [b] NH₃-TPD [c] Acid-base titration [d] Pyridine-FTIR.

Dealumination was performed using HCl and citric acid as these agents act differently in the matrix. The HCl, being a strong acid and small molecule, caused a decrease in acidity to a higher extent than the mild citric acid. The acidity drastically decreased from 0.59 to 0.24 mmolg⁻¹ for HCl due to its access towards more aluminium sites throughout the matrix. The B/L ratio decreased from 3.9 to 1.9 due to the removal of framework aluminium mainly decreasing the Brönsted acidity. In the case of citric acid, due to its mild acidity, extra framework aluminium (Lewis acid site) could be predominantly dealuminated. The total acidity decreased marginally from 0.59 to 0.53 mmolg⁻¹, whereas B/L ratio increased from 3.9 to 4.6 (Table 1, ESI Fig. S6). [33,34]

Phosphate treatment resulted in a decrease in total acidity affecting primarily the strong Brönsted acid sites (>350 °C). Upon an increase in the concentration of phosphate treatment from 1 to 5%, the acidity marginally decreased from 0.42 to 0.37 mmolg⁻¹ (Table 1) due to the generation of weaker phosphate type of acid sites. [27] The strong Brönsted acidity decreased from 0.22 to 0.08 mmolg⁻¹ for HZSM-5 upon an increase in the phosphate treatment from 0 to 5%. The phosphate treatment creates low strength P—O—H acidic sites by different types of interactions with framework Al sites. Certain interactions can cause the replacement of two Al acid sites by one P—O—H Brönsted acid site leading to a decrease in total acidity. For ZSM-5 with higher SAR, the total acidity might increase due to the enhanced acid site spacing, thus

creating more than one P—OH sites per Al site. This type of interaction of the phosphate group is more predominant for zeolite with closely positioned acid sites (lower SAR). [35–38]

The B/L ratio increased from 3.9 (HZSM-5) to 4.3 and 6.8 upon treatment with 1% and 3%P respectively. This shows that Al acid sites are converted into weaker -P–OH type acid sites. Further increase in phosphate to 5% decreased the B/L ratio which could be attributed to pore narrowing of the zeolite leading to blocking of accessibility to the pyridine probe molecule. (Table 1, ESI Fig. S6) [27,39]

Metal ion was exchanged with H^+ of HZSM-5 to induce Lewis acidity in the zeolite matrix. When copper and zinc ions were exchanged with the Brönsted acidic protons of ZSM-5, the Lewis acidity is expected to increase [40]. But the total acidity of HZSM-5 (0.59 mmol g⁻¹) was found to decrease to 0.48 and 0.45mmolg⁻¹ upon modification with Zn²⁺ and Cu²⁺ respectively due to the lowering of Brönsted acidity [ESI Fig. S5 (a)]. The B/L ratio decreased from 3.9 (HZSM-5) to 1.2 and 0.8 for Zn-ZSM-5 and Cu-ZSM-5 respectively as expected due to the incorporation of Lewis acidic metal centers (Table 1, ESI Fig. S6).

In the case of all the modifications on HZSM-5 (SAR95), it is observed that the strong acid sites were affected the most as there is a shift in the desorption peak towards lower temperature which is evident from the TPD profiles and acidity values (Table 1). NH₃-TPD studies were performed for all the catalysts tested which showed comparable results with



Fig. 2. Temperature programmed desorption profiles of (a) HZSM-5 with varied SAR [a-SAR22, b-SAR57 c-SAR95 d-SAR117 e-SAR160], (b) Desilicated ZSM-5 [a-HZSM-5(SAR95) b-DS (0.2 M NaOH) c-DS (0.1 M NaOH)] (c) Dealuminated ZSM-5 [a-HZSM-5(SAR95) b-DA (Citric acid), c-DA (HCl)] (d) Phosphate modified ZSM-5 [a-HZSM-5(SAR95), b-1%P-ZSM-5, c-3%P-ZSM-5, d-5%P-ZSM-5].

the literature [ESI Fig. S5 (b-g)] [28-30].

3.2. Catalytic activity studies

3.2.1. Catalyst screening and comparison

From the prior knowledge on the alcoholysis reaction, it is understood to be purely an acid catalyzed reaction and the Brönsted acid sites specifically play a major role in the selective synthesis of alkyl levulinate. Hence, various conventional solid acid catalysts like zeolites, mesoporous aluminosilicates, silicoaluminophosphate, cation exchange resin and sulfated zirconia were screened for this reaction. To know the essential qualities that are required in a catalyst to get maximum activity, the catalytic conversion and selectivity were correlated with their physicochemical properties.

Butanolysis of furfuryl alcohol to yield butyl levulinate was carried over various solid acid catalysts such as HZSM-5, Y-zeolite, H-Beta, mordenite, amberlyst-15, sulfated zirconia, SAPO-34 and Al-SBA-15. Prior to this study, a blank reaction was performed in the absence of the catalyst which gave a trace level conversion.

Amberlyst-15, a pure Brönsted acidic catalyst, gave the highest selectivity (92 %) for butyl levulinate followed by HZSM-5 (66 %) with conversions for both the catalysts near to completion. The better catalytic performance of amberlyst-15 catalyst can be attributed to the high number of Brönsted acidity present in it compared to any other catalyst

taken in this study. The HZSM-5 with its unique uniform medium-sized micropore structure as well as its strong Brönsted acid character might have helped in getting good performance for this reaction. The rest of the catalysts exhibited lower catalytic activity (< 20 %) as shown in Fig. 3. Mordenite having two channels (channel dimension: 0.70*0.65 and 0.57*0.26) behaves as a one-dimensional pore system as one of the pores restricts the movement of molecules, lowering its catalytic performance [41]. The low performances of the H-Beta and Y-zeolite show that the large pore structure may not be suitable for this reaction. H-Beta gave \geq 99 % furfuryl alcohol conversion, but the intermediate butoxy methyl furan (hereafter BMF) conversion into butyl levulinate was low. The presence of strong acidity in H-beta helped to achieve high conversion but resulted in high selectivity towards side products; BMF and 5,5-dibutoxy-2-pentanone. On the other hand, Y-zeolite exhibited poor conversion of furfuryl alcohol itself which may be due to the dominated presence of weak and moderate number of acid sites. Though SAPO-34 contained mainly weak and moderate acid sites with good surface area, the presence of weaker phosphate type groups could be the reason for its low furfuryl alcohol conversion (12 % at 6 h). Al-SBA-15 possessing mesoporosity, acidity in the broad range of 50–550 °C and high surface area gave > 99 % furfuryl alcohol conversion but its low selectivity towards butyl levulinate could be because of the low conversion of the intermediate BMF due to the weaker Al acid sites. Though sulfated zirconia possessed acid strength in the broad range of 50-550 °C,



Fig. 3. Catalyst screening. Reaction conditions: catalyst concentration-3 wt%, temperature-110 °C, mole ratio- 1:10 (furfuryl alcohol: butanol), reaction time- 6 h.



Fig. 4. (a) Effect of silica to alumina ratio (SAR) of HZSM-5 (b) Correlation of butyl levulinate selectivity with acidity. Reaction conditions: Catalyst concentration-3 wt%, temperature- 110 °C, mole ratio- 1:10 (furfuryl alcohol: butanol), reaction time- 6 h. For all the catalysts, furfuryl alcohol conversion \geq 99 %.

conversion of furfuryl alcohol was low (13 % at 6 h) which could be due to its smaller surface area and lower number of acidity compared to HZSM-5 (Table 1). Both Al-SBA-15 and sulfated zirconia gave a considerably high amount of 5,5-dibutoxy-2-pentanone side product with 11 and 5% selectivity respectively. Hence, we can conclude, in general, that pore size, strength and number of acid sites are largely responsible for the catalyst efficiency for this two-step tandem reaction.

Amberlyst-15 gave almost complete conversion and high selectivity for butyl levulinate. However, being an organic cation-exchange resin, it is always suspected about its performance in successive catalyst cycles. Due to its low thermal stability (120 °C), the calcination cannot be employed for the removal of the adsorbed substrate/product species which block the active sites. Therefore, recycling by repeated methanol washing and drying at 110 °C for 12 h was employed which, however, did not help in retaining its activity. It is found that there was a drastic decrease in activity from 92 to 22 % during the recyclability test (ESI Fig. S7). Hence, HZSM-5 with high thermal stability was opted for further studies which gave almost complete conversion and fairly high selectivity of 66 % for butyl levulinate.

3.2.2. Effect of SAR

As the change in SAR in zeolites results in the variation of number and strength of acidity, HZSM-5 with different SAR was investigated for alcoholysis of furfuryl alcohol with butanol. The conversion of all the HZSM-5 catalysts with the SAR ranging from 22 to 160, was above 95 % at 110 °C [Fig. 4(a)]. Interestingly, the selectivity towards butyl levulinate did not show any linearity with respect to the SARs. However, it should be marked that the high amount of acidity had less influence on the selectivity though the trend of the catalytic performance was a volcanic peak [Fig. 4(b)]. The order of the catalytic performance of the SARs in HZSM-5 with respect to selectivity (%) is SAR95 > SAR117 > SAR160 > SAR57 > SAR22. This trend may be due to the competing reactions leading to pore/ active site blockage making the reaction slower with time for HZSM-5 with lower SAR. Oligomerization is more prone in lower SAR catalysts due to the higher Brönsted acidity. In the case of higher SARs, low acid site density leads to low catalytic activity. A similar trend was reported for the different acid-catalyzed reaction using HZSM-5 [42]. Therefore, SAR95 seems to be the optimal catalyst that favors efficient production of butyl levulinate compared to the rest. To explore the nature and to understand the active sites responsible for the transformation, the catalyst with the highest catalytic selectivity of 66 %, HZSM-5 (SAR95) was post modified by desilication, dealumination, metal-ion exchange and phosphate modification were screened for this reaction.

3.2.3. Catalytic activity studies for post synthetically modified HZSM-5

The butanolysis reaction of furfuryl alcohol with butanol was conducted using post synthetically modified HZSM-5 (SAR95) by desilication and dealumination using 0.1 M, 0.2 M NaOH and citric acid/ HCl respectively. The alkali treatment was restricted to 0.2 M NaOH concentration as it lowers the crystallinity of the material upon an increase in the concentration \geq 0.5 M which would lead to the destruction of the framework resulting in the partial/complete collapse of the zeolite structure [32]. These modifications resulted in a decrease of butyl



Fig. 5. Catalyst performance of HZSM-5 (SAR 95) upon post modification (a) Desilication (b) Dealumination (c) Phosphate modification (d) Metal ion exchange. Reaction conditions: Catalyst concentration- 3 wt%, temperature- 110 °C, mole ratio- 1:10 (furfuryl alcohol: butanol), reaction time- 6 h. Furfuryl alcohol conversions for all the reactions \geq 99 %.

levulinate selectivity in the range of 55–42 % compared with parent HZSM-5 (SAR95) (66.6 %) which could be due to the lowering of number and strength of acidity [Fig. 5 (a) and 5(b)]. As the conversion level after modifications were almost similar (>99 %), it implies that the conversion of intermediate BMF to butyl levulinate is mainly affected by these modifications [ESI Fig. S8 (a, b)].

Upon treatment of varied concentration of phosphate, the catalysts were tested to explore the role of weaker acid sites on the reaction. It was found that with an increase in the phosphate treatment the selectivity towards butyl levulinate drastically decreased from 53.2–30.9 % [Fig. 5 (c)]. This is due to the decrease in the concentration of strong Brönsted acidity which was replaced by weaker acid sites upon phosphate treatment as expressed in the TPD profile [27]. In the TPD profile of the highest phosphate modification (5% P-ZSM-5), strong Brönsted acid sites diminished after the treatment which explains its poor performance [Fig. 2(d)]. This proves the necessity of a sufficient number of strong Brönsted acidity for this transformation.

The Zn^{2+} and Cu^{2+} ions were exchanged with HZSM-5 (SAR95) to understand the role of Lewis acidity on the reaction. While the two modified catalysts retained almost complete conversion, butyl levulinate selectivity decreased with respect to the parent HZSM-5. The initial formation of butyl levulinate of Cu-ZSM-5 and Zn-ZSM-5 till 2 h was close to that of parent HZSM-5 after which the gap between them increased indicating the poorer conversion of BMF intermediate to the product at higher reaction time compared to parent HZSM-5 [ESI Fig. S8 (d)]. The overall decrease in the selectivity of parent HZSM-5 from 66.6-50.6 % (Zn-ZSM-5) and 49.1 % (Cu-ZSM-5) could be due to decrease in number and strength of acid sites [Table 1, Fig. 5(d)].

3.2.4. Influence of reaction conditions

Among all the well-known solid acids and acidity-structure modified ZSM-5 catalysts, HZSM-5 (SAR95) that showed the highest efficiency was selected to study the influence reaction parameters such as catalyst concentration, reactants mole ratio and temperature.

3.2.4.1. Effect of catalyst concentration. The effect of the catalyst loading ranging from 0.75 to 3.75 wt% (with respect to total reactants)

was studied with HZSM-5 (SAR95) as shown in Fig. 6 (a). It is observed that the variation in catalyst loading had a pronounced effect on the butyl levulinate selectivity. The selectivity increased substantially from 25.3-66.6 % with an increase in the catalyst loading from 0.75 to 3 wt%. At a lower catalyst loading, though the conversion of furfuryl alcohol was not affected (≥ 99 % at 6 h), it is observed that the BMF (intermediate) conversion was lower, thereby affecting the butyl levulinate selectivity. Hence, the first transformation of furfuryl alcohol to intermediate BMF occurs easily with a low amount of the catalyst, whereas the second transformation of the intermediate to butyl levulinate requires higher catalyst amount [ESI Fig. S9 (a)]. With further increase in the catalyst loading to 3.75 wt%, the selectivity of butyl levulinate decreased as the product concentration was distributed mainly over BMF and other side product, 5,5-dibutoxy-2-pentanone. As the reaction demands a minimum of 3 wt % catalyst loading, which is less compared with that used in most of the previous reports, the catalyst concentration of HZSM-5 (SAR95) was fixed to 3 wt% for further studies.

3.2.4.2. Effect of reactants mole ratio. Since this reaction involves substrate, furfuryl alcohol which is prone to polymerization, the other substrate concentration (butanol) becomes important. Butanol not only takes part in the alcoholysis but, at the same time, also reduces the formation of polymeric side products by acting as a solvent or a diluent. Thus, the optimized mole ratio (furfuryl alcohol: butanol) helps in reducing the furfuryl alcohol side reactions thereby affectively avoiding catalyst poisoning. Though the conversion of furfuryl alcohol was not altered (\geq 99 %) by varying the mole ratio, butyl levulinate selectivity was mainly influenced by it. At lower molar ratios from furfuryl alcohol: butanol, 1:2.5 to 1:7.5, the butyl levulinate selectivity was not much changed (45–47%) [Fig. 6(b)]. However, upon increasing the mole ratio from 1:7.5 to 1:10, the selectivity of butyl levulinate was enhanced by 20 % (66.6 %). Further increase in the mole ratio to 1: 12.5 and 1:15, the selectivity considerably decreased (51-48 %) which might be due to the partial blockage of active sites for the intermediate BMF to react further by excess butanol that predominantly resides on the active sites being more polar compared to the ether (BMF) [ESI Fig. S9 (b)]. Hence this study confirms that furfuryl alcohol to butanol ratio of 1:10 is the



Fig. 6. Influence of reaction conditions. (a) Effect of catalyst loading : Reaction conditions: Temperature- 110 °C, mole ratio- 1:10 (furfuryl alcohol: butanol), reaction time- 6 h. (b) Effect of reactants mole ratio: Reaction conditions: Catalyst concentration- 200 mg, temperature- 110 °C, reaction time- 6 h. (c) Effect of reactants mole ratio: Reaction conditions: Catalyst concentration- 200 mg, temperature- 110 °C, reaction time- 6 h. (c) Effect of reactants mole ratio: Reaction conditions: Catalyst concentration- 1:10 (furfuryl alcohol: butanol), reaction time- 6 h. Furfuryl alcohol conversions for all the reactions \geq 99 %.

optimal stoichiometric mole ratio for this reaction.

3.2.4.3. Effect of reaction temperature. Effect of temperature on the alcoholysis of furfuryl alcohol was investigated in the temperature range of 90-117 °C in the batch mode while keeping other parameters constant [Fig. 6 (c)]. Though the temperature change did not affect the furfuryl alcohol conversion (> 99 % at all temperatures), there was a visible impact on the selectivity of butyl levulinate. In the case of temperature 90 and 100 °C, though the intermediate BMF formed was considerably high in concentration (73 %) compared to 110 °C (67 %), the conversion of BMF to butyl levulinate over the time was slower (48 % for 90 °C and 53 % for 100 °C). At temperature 110 °C, the selectivity towards butyl levulinate improved to 66.6 % due to an appreciable decrease in BMF concentration from 67 to 20 % [ESI Fig. S9 (c)]. Further increase in temperature to 117 °C, decreased the butyl levulinate selectivity by 8.9 % (to 57.7 %). Hence at 110 °C, the reaction was suitable for higher butyl levulinate selectivity. Therefore, after the complete investigation on the reaction parameters, the optimized temperature, the mole ratio of furfuryl alcohol to butanol and catalyst concentration are 110 °C, 1:10, and 3 wt% respectively.

3.2.5. Catalyst recyclability study

To investigate the catalyst stability towards multiple cycles, experiments were conducted by regenerating the catalyst in between the four cycles under the optimized conditions (Fig. 7). During each cycle, the catalyst demonstrated almost the same catalytic activity as that of the fresh catalyst. This implies that there was no loss of any active sites during reaction or in the regeneration process which was reflected at the spent catalyst characterization. This proves HZSM-5 (SAR95) to be a highly potential catalyst for alcoholysis reaction as it addresses all the drawbacks of the reported catalysts such as poor recyclability, the need of high catalyst loading and butanol requirement, high cost of the catalyst and difficult synthesis procedures.

3.2.6. Time resolved study

Time resolved study was carried out for the alcoholysis of furfuryl alcohol for 24 h using HZSM-5 (SAR95) catalyst under the optimized conditions. The catalyst showed ≥ 99 % furfuryl alcohol conversion within an hour and the selectivity towards the intermediate BMF decreased from 67 (15 min) to 1.9 % with an increase in time to 24 h. During the reaction, the butyl levulinate selectivity reached 24 % in 15 min and then increased rapidly to 66 % in 6 h, but then took more time to finally attain 85 % in 24 h (Fig. 8). This suggests that there was a slow conversion of the intermediate, BMF to butyl levulinate after 6 h which may be attributed to the active site saturation with products in the course of time. The increase in the butyl levulinate selectivity with time



Fig. 8. Time resolved study. Reaction conditions: Catalyst concentration- 3 wt %, temperature- 110 $^{\circ}$ C, mole ratio- 1:10 (furfuryl alcohol: butanol), reaction time- 24 h.

also demonstrates the progressive performance of the catalyst with time by efficiently converting the intermediate BMF to the desired product which proves that this is a consecutive reaction.

Under the optimized reaction conditions, the HZSM-5 (SAR 95) gave 99 % conversion and 85 % selectivity in 24 h. This catalyst activity was compared with other reported catalysts from the literature. The catalyst performed well under milder reaction conditions (lesser catalyst loading and a lower mole ratio of the reactants) and excellent recyclability in comparison with most of the reported catalysts (ESI Table S2).

3.2.7. Plausible reaction mechanism

The plausible mechanistic pathway of alcoholysis of furfuryl alcohol to form alkyl levulinate is proposed in Scheme 2. The reaction proceeds by the formation of an intermediate alkoxy methyl furan which then gets transformed to 2-alkoxy-5-methylene-2,5-dihydrofuran by 1,4 addition of the alcohol. Ring-opening occurs by subsequent production of alkyl levulinate [43]

3.2.8. Substrate scope study

Due to the vast applications of various alkyl levulinates, it is interesting to explore the catalytic performance of HZSM-5 (SAR95) catalyst using various alkyl alcohols. Hence, the effect of the substrate was evaluated for alcoholysis of furfuryl alcohol to yield methyl levulinate, ethyl levulinate, propyl levulinate and butyl levulinate at the reflux temperature. Under optimized conditions, the conversion of furfuryl alcohol, irrespective of the alcohols used, was >95 % and the selectivity



Fig. 7. Catalyst recyclability study. Reaction Conditions: temperature: 110 °C, catalyst concentration- 3 wt%, mole ratio- 1:10 (furfuryl alcohol: butanol), reaction time- 6 h.



Scheme 2. Plausible mechanistic pathway for the alcoholysis of furfuryl alcohol to yield alkyl levulinate.

towards the product increased with an increase in the alkyl chain of the alcohol in the following order methanol < ethanol < propanol < butanol (Fig. 9). At its reflux temperature, when methanol was employed, the selectivity towards the intermediate methoxy methyl furan (MMF) and other side products were 50.2 and 35.5 % respectively. This clearly explains the low selectivity of methyl levulinate (14.3 %) during the reaction. In the case of ethanolysis of furfuryl alcohol, the selectivity for ethyl levulinate was 20.7 % for 6 h reaction. The ethoxy methyl furan (EMF) and the other side products were formed with a selectivity of 55.6 and 23.7 % respectively. Reactions for propyl levulinate and butyl levulinate synthesis resulted in 50.3 and 66.6 % selectivities for these products respectively under reflux temperature. This trend could be due to the + I effect of the alkyl group guiding the conversion of the intermediate (alkoxy methyl furan) to its respective products (ESI Fig. S10). Therefore, as the alkyl chain in the alcohol is increased, the conversion of the intermediate is enhanced, thereby increasing the selectivity towards the alkyl levulinate.

4. Conclusions

Zeolites being one of the classic materials are still startling the scientists by its flexible material properties and promising catalytic activities in many important and challenging transformations. In alcoholysis of furfuryl alcohol which was efficiently converted into butyl levulinate with the aid of HZSM-5 (SAR95) in a batch regime proved the exclusive requirement of the uniform medium size micropore structure, high surface area, strong Brönsted acidity, optimal number of acid sites and good thermal stability for this reaction. The combination of the properties inherited by the HZSM-5 with the tuning of acidity makes it different from the other catalysts. Considering the green chemistry principles such as moderate experimental conditions, excellent reusability, low reactants mole ratio and catalyst concentration, HZSM-5 (SAR95) proves to be the best candidate for this transformation as it addresses all the drawbacks of the reported catalysts.



Fig. 9. Effect of alkyl chain on alcoholysis. Reaction Conditions: Catalyst-HZSM-5 (SAR95), temperature: Reflux condition, catalyst concentration-200 mg, mole ratio- 1:10 (furfuryl alcohol: alcohol), reaction time- 6 h. The fur-furyl alcohol conversion of all the substrates >95 %.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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