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catalyst for selective synthesis of ethyl levulinate from furfuryl alcohol

Magnetically separable sulfated zirconia as highly active acidic

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Magnetically separable sulfated zirconia catalysts were prepared by a two-step approach. Coating of zirconia around the particles helps to increase the number of sites needed for the sulfate ion loading and hence enhances the acidity of catalyst. Different molar concentration of chlorosulfonic acid was used for sulfonation. The prepared catalysts were used for selective synthesis of ethyl levulinate using renewable substrates: furfuryl alcohol and ethanol. Ethyl lavuliante has many applications in different industries including a potenital blending component in biodiesel. The catalyst could be easily separated by the use of magnet. Influence of different parameters was investigated to reach the optimum yield of ethyl levulinate. The detailed kinetics was established for scale up purposes. The catalyst is robust and reusable.

### Introduction

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Biomass derived chemicals have several applicationsin many important industries such as pharmaceutical, fine chemical intermediate and fuel additive, etc.<sup>1-3</sup>One of the major and green parts of utilization of biomass is in the field of biofuel production eitheras intermediate or as additive.<sup>4</sup>Continuous efforts are expended to synthesize these fuel additives using direct biomass or derived chemicals. However, efficient methods and economical way of synthesis are still lagging. The catalytic conversion of biomass/derivatives would be a good option to achieve economical processes. Carbohydrates and the derived molecules have a great potential to be converted into fuels and chemicals as they are abundant and cost effective.<sup>1</sup>The potential uses of levulinic acid and its derivatives in several industries make it one of the important

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value added chemicals derived from the biomass.<sup>5</sup>There are several synthetic processes of levulinic acid production from carbohydrates (i.e. glucose, fructose, sucrose) and utilization of biomass such as starch, wood, agricultural waste and grain sorghum using homogeneous and heterogeneous catalysis has been reported.<sup>6</sup>

Alkyl levulinate esters have potential uses in flavour and fragrance industries and can be effectively used as blending components in biodiesel and plasticizers, solvents, etc.<sup>5-7</sup> Usually these esters are synthesized by levulinic acid esterification using different acid catalysts with alcohols, but the high cost of levulinic acid makes the processes uneconomical.<sup>6</sup>Alternatively, several acid catalysed processes have been reported to obtain alkyl levulinates with different biomass resources such as HMF, cellulose, carbohydrates, and furfuryl alcohol with corresponding alkyl alcohols.<sup>7-9</sup>The basic conclusion with the use of acid catalysts in all processes is that the amount and acidic strength of catalyst plays a vital role to achieve better yields of alkyl levulinate. Therefore, the right combination of a suitable feedstock and catalyst is desirable to achieve this goal. The oversupply of furfuryl

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alcohol (FAL) and its underutilization in the chemical market, makes it a promising molecule to be converted into a high value added products such as fuel additive i.e. alkyl levulinates from low value added product FAL.<sup>6</sup>Several homogeneous catalysts such as mineral acids (H<sub>2</sub>SO<sub>4</sub>, HF and H<sub>3</sub>PO<sub>4</sub>) and heterogeneous solid acids and super acids catalysts, namely, zeolites, mesoporous aluminosilicates Al-TUD-1, mixed acids, sulfated zirconia, sulfonic resins, sulfonic acid containing ionic liquids, ion exchange resins, and organic-inorganic hybrid acids were used for the efficient synthesis of alkyl levulinate.<sup>6,9-16</sup> However, several disadvantages associated with these catalysts such as catalyst separation, reusability, thermal stability, activity loss, mass transfer resistance and high cost still present formidable challenges to be overcome. Thus, designing cheaper and environmental benign catalysts is the solution.

Heterogeneous catalysts are supposed to play a key role in development of environment friendly processes and technology. Among the various solid acid and super acid catalysts, sulfated metal oxide catalysts are more interesting because of their high acidity and excellent thermal stability and reusability, leading to different reactor configurations.<sup>17</sup>Various metal oxides such as ZrO<sub>2</sub>, TiO<sub>2</sub> and SnO<sub>2</sub>, mesoporous materials, etc. have been used for this purpose, among which sulfated zirconia (SZ) has been reported to retain more amount of sulfur as compared to other supports and resulting in highly acidic catalyst.<sup>18</sup>Sulfated zirconia was used in several industrially important reactions such as esterification, Friedel-Craft reactions, condensation, and many more usual acid-catalysed oligomerisation, reactions.17-22We have developed a novel approach of preparation of high acidic sulfated zirconia named as UDCaT-5<sup>18</sup> and FLSZ<sup>19</sup> with the retention of tetragonal phase of zirconia having more than 4% of sulfur loading by using chlorosulfonic acid as thesulfating agent. The use of chlorosulfonic acid results in the high acidic value and complete phase transformation of zirconia was successfully avoided which helps to get the high activity as compared to those using sulfuric acid treatment. Use of magnetically separable catalyst has attracted overwhelming attention in recent years because of the ease of separation from the reaction mass using simple magnetic field. Also the nonreactive nature, cheap source and ease of preparation make it very attractive to be used in synthesis of heterogeneous catalysts. <sup>23, 24</sup> DOI: 10.1039/C6GC02466A

There are several methods to prepare a magnetically separable solid acid catalyst, either by attaching sulfonic acid group to magnetic particle or to the mesoporous material coated on the magnetic particles.<sup>23-26</sup>However, the acidity possessed by these catalysts is not high as compared to the metal oxide supported acidic catalysts; also they are highly moisture sensitive vis-a-vis sulfated metal oxides catalysts. So far no detailed reports have been published on zirconia coated on hydrothermally prepared magnetic particles and their sulfonationusing chlorosulfonic acid to get the magnetically separable sulfated zirconia.

In this work, we have successfully synthesized sulfated zirconia coated on  $Fe_3O_4$  particle and its application to synthesis of high valuable ethyl levulinate from furfuryl alcohol. The catalyst was fully characterized by several characterization techniques, before and after reuse. Detailed kinetic study has been reported first time. The process is green and novel.

#### **Experimental section**

#### Materials

Zirconium oxychloride, aq. ammonia solution, chlorosulfonic acid and furfuryl alcohol were bought from SD Fine Chem. Ltd. Mumbai, India. Ferric chloride, ferrous chloride and ethanol were purchased from Thomas Baker, Mumbai.

#### **Catalyst Synthesis**

The synthesis of the catalyst was divided in two parts. First, the preparation of the magnetic particles (F) and coating of the zirconium hydroxide on the particle was achieved to get zirconium hydroxide coated magnetic particle (Zr (OH)  $_4$ F) and second was the acid treatment to get the magnetically separable solid acid catalyst. The synthesis of the magnetically separable sulfated zirconia (SZF) is illustrated in Figure 1.

The magnetic nanoparticles were synthesized by hydrothermal method as reported by Deng et al.<sup>27</sup>It was reported as a cheap, simple and one step method to get the monodispersed magnetic particles. The synthesis of magnetic particle (F) is as follow: 25 ml of ethylene glycol was taken in beaker and to this FeCl<sub>3</sub>.6H<sub>2</sub>O (2.5 mmol, 0.68 g) and NaOAc.3H<sub>2</sub>O (13 mmol, 1.8 g) were added and stirred for 30

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min to form homogeneous mixture and then transferred to the Teflon lined bomb reactor (100 ml).



Fig.1:Synthesis of magnetically separable sulfated zirconia (SZF)

The reactor was then transferred to muffle furnace and heated to 200°C for 24 h. The reactor was cooled down to 30°C, magnetic particles collected, washed with ethanol to remove unreacted material and dried at 100°C for 12 h. The magnetic particles were then subjected to zirconium coating by using zirconium oxychloride as precursor. One g magnetic particles were sonicated to get dispersed material in 50 ml deionized water. Aqueous solution of zirconium oxychloride and ammonia was then added drop wise to the dispersed magnetic particles. The pH was maintained around 9-10 and stirred for 3 h. The solid material was collected by using external magnet and washed several times with deionised water to get the Zr(OH)<sub>4</sub> coated magnetic particle (Zr(OH)<sub>4</sub>-F).The AgNO<sub>3</sub> test was used to confirm the complete removal of chloride ions. The synthesized particles were dried at 120°C for 24 h.

The prepared magnetically separable material  $Zr(OH)_4$ -F was then subjected to the chlorosulfonic treatment to get the active sulfated zirconia coated on magnetic particle (SZF) catalyst. The procedure is as follow: zirconium hydroxide coated magnetic particle was sulfonated by immersing the material in 15 cm<sup>3</sup>/g of three different molar concentration (0.5M, 1M and 2M) of chlorosulfonic acid in ethylene chloride. The material was quickly transferred to oven at 1200 °C and kept for 24 h. It was calcined at 650°C for 5 ft. Three different catalysts so prepared are designated as 0.5M-SZF, 1M-SZF and 2M-SZF, respectively. The sulfonated Fe<sub>3</sub>O<sub>4</sub> (SF) particle was prepared by immersing the prepared magnetic particle in 15 ml/g 1 M chlorosulfonic acid in ethylene chloride and rest of the procedure was the same as described above. UDCaT-5, FLSZ and Cs-DTP/K-10 catalysts was prepared by the methods reported earlier.<sup>18, 19, <sup>28</sup>Zirconium hydroxide coated magnetic particle was also calcined at 650°C to prepare ZrO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>particle noted as ZF.</sup>

#### **Characterization of catalysts**

Catalysts were characterized by various techniques<sup>28, 29</sup> and details are provided in Supplementary Information.

#### **Reaction procedure**

The reactions were conducted in stainless steel 100 ml autoclave with four blades- pitched turbine impeller and PIDcontrolled heating arrangement (Amar Equipments Mumbai). The calculated amount of reactants was fed to the reactor along with the internal standard (3 % v/v) and desired amount of catalyst. The desired temperature was set by using a digital temperature setup. In a particular reaction, 0.048 mol furfuryl alcohol, 0.72 mol ethanol and 0.3 mL n-dodecane (internal standard) were taken with catalyst loading of 7.5 g/L. Once the temperature reached the set value, the reaction mixture was stirred for 1 min and initial sample was collected. Samples were collected at specified time intervals for analysis at the desired stirring speed. The catalyst particles present in collected samples were magnetically separated by external magnet and the liquid was transferred to another vial and then analysed by GC (Chemito-1000) having a BP-1 capillary column and FID detector.

#### **Results and Discussion**

#### BET surface area analysis

The nitrogen adsorption-desorption isotherm of sulfated catalyst and zirconia coated magnetic particle was recorded to get surface area (S.A.) and pore volume (P.V.) of the prepared sample (Table 1). Zirconium oxide coated magnetic particles (ZF) and the sulfated catalysts show that the pore diameters in the mesoporous material range (i.e. between 2 nm to 50 nm). The hysteresis loop shown in Figure 2 further confirms that the prepared catalysts are mesoporous in nature. The micropore volumes of all samples are almost negligible,

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which further confirms mesoporous nature of catalyst samples. As reported earlier; with increase in sulfur loading, the surface area first increases (119  $m^2/g$ ) up to 4 % w/w sulfate content and then suddenly decreases to 71  $m^2/g$  at 5.6% w/w sulfate content which is attributed to the sulfate ion migration from the surface to the bulk phase.<sup>18,22</sup> The surface area of ZF decreases after sulfonation. The decrease in surface area and pore volume of the sulfated catalyst confirms the successful grafting of sulfate ions on the zirconia coated magnetic particle. Further catalysts treated with different concentration of chlorosulfonic acid show that on increasing the concentration of chlorosulfonic acid it results in decrease in surface area and pore volume. It indicates that more sulfate ions have been moved to the bulk phase of the catalyst. The magnetic particles after zirconia coating show typical mesoporous nature due to the zirconia on the surface. Even though the sulfonation of these particles decreases the overall surface area and pore volume of the catalyst, it does not affect the mesoporous nature (Figure 2).Reused catalyst shows slight increase in the surface area and pore volume which may be due to leaching of a few sulfate ions.



Fig. 2:  $N_2$  adsorption-desorption isotherms of (a) ZF, (b) 1M-SZF, (c) Reused 1M-SZF (d) 2M-SZF

#### X-ray powder diffraction (XRD)

XRD patterns of ZF and sulfated catalyst (1M-SZF) have been recorded. The magnetic particles show distinct peaks at  $2\theta$  values of 30.2, 35.6, 43.3, 57.84, and 63.1 which are ascribed to (220), (311), (400), (511) and (440) planes of





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Fig.3 XRD of different catalysts (a)  $Fe_3O_4$  particles, (b) ZF, (c) 1M-SZF, (d) Reused 1M-SZF .

 Table 1: Surface area pore volume and pore diameter properties

 of different catalysts

Sr. No	Catalyst	Surface area (m²/g)	Pore diameter (nm)	Pore Volume (cm <sup>3</sup> /g)
1	ZF	51.6	17.2	0.23
2	0.5M-SZF	31.9	20.9	0.16
2	1M-SZF	13.7	22.1	0.06
3	2M-SZF	7.9	24.9	0.05
3	Reused 1M-SZF	16.26	22.8	0.07

#### Fourier transforms infrared spectroscopy (FT-IR)

The nature of surface retained sulfur and acidic sites generated on the surface was studied by using FTIR spectroscopy (Figure 4). For the magnetic particles, the vibration band at v = 580 cm<sup>-1</sup> corresponds to Fe-O vibration. The zirconia coated magnetic particle shows a characteristic peak between 450 and 750 cm<sup>-1</sup> related to zirconium oxide and to magnetic particles present in the material. The sulfated catalyst (1M-SZF) shows the characteristic peaks at 1320, 1280, 1124.47, 1009.65, and 972 cm<sup>-1</sup> related to the zirconia coordinated bidentate sulfate ion  $(-SO_4^{-})$ . The peak at cm<sup>-1</sup> 1445 corresponding to the presence of polynulclearsulfates on the surface of the catalyst was not noticed in the IR spectra which confirms the absence of the  $S_2O_7^{2-1}$  ions. The IR peaks at 1637 cm<sup>-1</sup> is due to the presence of water molecule associated with sulfate group.<sup>30</sup>These molecules are supposed to be present due to the decomposition of chlorosulfonic acid during calcination of catalyst and hence it confirms the absence of chlorosulfonic acid in the catalyst and retention of sulfate ion on the surface of the catalyst. The band at 3450 cm<sup>-1</sup> is due to the vibration caused by the presence of the free OH group. The fresh catalyst and used catalyst show no difference in the spectra except a small decrease in intensity after reuse.

#### **TGA** analysis

The TGA analysis of the samples helps to check the thermal stability and to find out the amount of the sulfur



retain by the 1M-SZF after the calcination temperature (i.e. 650 °C)



**Fig 4**FT-IR spectra of catalysts (a) Fe<sub>3</sub>O<sub>4</sub> particles, (b) ZF, (c) 1M-SZF, (d) Reused 1M-SZF.

(Figure 5). The DSC-TGA profile of Zr (OH) 4-F shows two stages of weight loss; first loss below 200°C and second between 200 and 550°C. The first weight loss is assigned to the removal of surface adsorbed water while the second loss corresponds to the terminal hydroxyl group removal which are bonded to zirconia surface (Figure 5 a).<sup>31</sup>Thereafter, it shows very less decrease in weight, of about 2.5% and hence it indicates that the structure is stable (up to 700°C). Exothermic peak seen at 530 °C can be assigned to the crystallization phenomena.<sup>31</sup>This peak is due to amorphous phase getting transformed in to the tetragonal phase of zirconia. The DSC-TGA profile of the sulfated ZrOH<sub>4</sub>-F shows a similar pattern of weight loss as seen in ZrOH<sub>4</sub>-F up to 600 °C. This loss in weight is because of removal of moisture and other adsorbed species. Endothermic peak around seen at 210 °C is due to the removal of solvent ethylene chloride in the sulfonation process.<sup>31</sup> The amount of sulfur retained by the material after calcination was calculated by TGA analysis in the temperature range of 650 °C to 700°C since the weight loss was mainly due to the decomposition of sulfates<sup>32</sup> and there is no weight loss seen in the case of the zirconia coated magnetic particle. The weight loss between 650 and 700°C is about 11% which indicates that such high sulfur content of the catalyst was present even after 650°C calcination temperature. Hence it is

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concluded that the catalyst possesses a good amount of sulfur needed for high activity of the catalyst.



Fig.5 DSC-TGA analysis of (a)  $Zr(OH)_4$ -F, (b) Sulfated  $Zr(OH)_4$ -F

#### NH<sub>3</sub>-TPD

The NH<sub>3</sub> –TPD characterization of different samples was done from 100 to 650°C and the total acidity was calculated in terms of mmol of ammonia (Table 2, Figure 6). ZF shows a very low acidic strength which may be due to the amphoteric nature of zirconia along with magnetic particles. Different ammonia desorption peaks in the range of 150 - $400^{\circ}$ C (weak acidic sites), 400-550°C (moderate acidic sites) and > 550°C (strong acidic sites), could be found easily in the magnetically separable zirconia catalyst after sulfonation. The sulfate groups present in the material generate strong Lewis and Bronsted acidic sites. The ammonia desorption peak at 627°C in the sulfated material is due to the presence of strongest Lewis acidic sites as reported by Barthos et





Fig. 6:  $NH_{3}$ - TPD patterns of different catalysts (a) ZF, (b) SF,(c) 0.5M-SZF (d) 1 M-SZF (e) 2 M-SZF (f) Reused 1M-SZF.

#### Table 2: Acid strength distribution of different catalysts

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No	Catalyst	Acidity (mmol/g)				
		Weak	Moderate/Strong	Total		
1	ZF	0.2		0.2		
2	SF	0.11	0.12	0.23		
3	0.5M-SZF	0.18	0.54	0.72		
4	1M-SZF	0.20	0.74	0.94		
5	2M-SZF	0.10	1.01	1.11		
6	UDCaT-5	0.30	0.23	0.53		
7	FLSZ	0.26	0.34	0.60		
8	1 <sup>st</sup> reused 1M-SZF	0.16	0.73	0.89		
9	2 <sup>nd</sup> reused 1M-SZF	0.17	0.67	0.84		
10	4 <sup>th</sup> reused 1M-SZF	0.16	0.69	0.85		
11	8 <sup>th</sup> reused 1M-SZF	0.15	0.64	0.79		

#### SEM analysis

The SEM images 1M-SZF is shown in Figure 7.The formation of small and large sulfated particles can be easily seen in the images. The particles are well distributed with irregular shapes and agglomerations of particles can be easily seen.The similarity in the external morphology of both the reused and virgin catalysts confirms that the structure remained intact during the reaction and after the regeneration. Hence the catalyst is robust and reusable.

The sulfonation does not affect the external morphology. The average particle size are in the range of 12-20 nm. The diffraction pattern of ZF (Figure 8 (a)) confirms the crystalline nature of material as the same in XRD, while after sulfonation the crystallinity decreases as evidenced in both TEM (Figure 8 (d)) and XRD. The well-defined patterns corresponds to different phases of zirconia and magnetic particles. The loss of crystallinity is due to the high loading of sulfur (here, ~10%), which is reported to be the main reason for the loss in crystallinity of catalyst. <sup>17, 22</sup>



#### (a)

(b)

Fig.7: SEM Images of (a, b) 1M-SZF (c) Reused 1M-SZF

#### **TEM analysis**

The TEM images of ZF and 1M-SZF reveal that there is a coating of the zirconia around the magnetic particles and thus the magnetic property is introduced in the catalysts (Figure 8).



Fig.8 TEM images of (a,b) ZF, (c,d) 1M-SZF

(c)

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(d)

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#### **Magnetic Properties of prepared catalyst**

To confirm the magnetic property of the catalyst, sulfated catalyst was dispersed in methanol taken in vials to form brown dispersion (Figure 9). This dispersed material was then brought into the magnetic field which was applied by using an external magnet or magnetic needle bar and within a few seconds the sulfated magnetic particles (SF) were completely gathered on the wall of the vial or on the magnetic needle as shown in Figure 9, resulting in the clear and transparent methanol solution. This confirms the magnetic nature of catalyst.



**Fig.9** Magnetic separation of the 1M-SZF catalysts; (a) dispersed in Methanol and (b, c) in the presence of magnetic force.

Further, to see the effect of zirconia loading and degree of sulfonation on the magnitude of magnetization of prepared samples, 3 different reaction vials were used and dispersed a calculated amount of different materials (i.e. magnetic particle (F), ZF and 1M-SZF) in 5 ml of methanol. Then the dispersed magnetic particle (F) were brought in contact of the magnetic field and within 26 s all the particles gathered at the side wall of reaction vials. The same procedure was employed for the other two samples and the time of accumulation of the materials was increased up to 43 s and 120 s, respectively. The magnitude of magnetization of the coated Fe<sub>3</sub>O<sub>4</sub> particle decreased after the coating of nonmagnetic material on the Fe<sub>3</sub>O<sub>4</sub> particle and is due to quenching of surface moments as explained by Xu et al.<sup>34</sup>

Since the magnetic particles were coated by the nonmagnetic materials such as zirconia and sulfur group, similar explanation can also be applied here. This results into decrease in the magnitude of magnetism and hence the nonmagnetic material coated  $Fe_3O_4$  particles (ZF and SZF) takes more time for accumulation as compared to the  $Fe_3O_4$  particles. Similarly, we have evaluated the we effect only for the samples. Similarly, we have evaluated the we effect only for the sample of the sample. Hence it is concluded that increase in concentration of concentration of the sample. Hence it is acid introduces more sulfate ions which results in decrease in magnitude of magnetization.

#### Efficacy of prepared catalysts

The prepared catalysts were employed for the synthesis of the ethyl levulinate. Furfuryl alcohol conversion to ethyl levulinate is a two-step process, in which first furfuryl alcohol reacts with ethanol to form intermediate and this intermediate is further converted into the ethyl levulinate (Scheme 1). Therefore, overall GC yield of the ethyl levulinate with time was considered for screening different catalysts which included 20% (w/w) Cs-DTP/K-10 (Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> supported K-10), FLSZ (Fuel lean sulfated zirconia), UDCaT-5 (modified mesoporous sulfated zirconia), Sulfated Magnetic particle (SF) and different magnetically separable sulfated catalysts (SZF) as described above. The yield of ethyl levulinate was calculated after 2 h ((Figure10). 20% w/w Cs-DTP/K-10 was found to be the least active for the reaction and gave 10% yield after 2 h while the sulfated catalyst showed better activity. The magnetically separable sulfated zirconia catalyst shows the highest activity as compared to the other catalysts used in the system. 1 M-SZF shows the 96% yield of the ethyl levulinate after 2 h with 100% conversion of furfuryl alcohol at 120°C. The increase in concentration of chlorosulfonic acid (0.5M-1M) in the treatment results in the high yield of the ethyl levulinate (Figure 10). However, as the concentration of the chlorosulfonic acid is increased from 1 to 2 M, there is hardly any change in the overall yield of the ethyl levulinate. 2M-SZF has more acidity, but as shown in surface area analysis the large amount of sulfate ions are present in the bulk of the catalyst and not on the surface and hence limits the access of the catalytic sites for the reaction. The reaction seems to be

strongly on the amount of acidic sites

present, which is being already been described by different

dependent

authors.6,8,11

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To confirm it, activity of various catalysts were correlated with the NH<sub>3</sub>-TPD analysis, which shows that the increase in acid strength of the catalyst results in increases in the yield of EL. The detail discussion about the amount of acidity possessed by these catalysts were already described in NH<sub>3</sub>-TPD section of characterization part. Table 2shows that the total acidity of different catalysts is in following order: SF (least)<UDCaT-5<FLSZ<0.5M-SZF<1M-SZF  $\approx$  2M-SZF (max). The activity of these catalysts is also in the same order. Hence 1M-SZF catalyst was chosen for parameter optimization to get the best possible yield of EL.

We have also compared the activity of different heterogeneous catalyst for synthesis of EL from LA and FAL (Table3). In the synthesis of EL from LA, very high temperature and long reaction time requires to get a good yield of EL as compared to the process reported with FAL and hence FAL is a better choice for synthesis.Further we have also compared activity of different heterogonous catalyst with our prepared catalyst. Long reaction time, high temperature, high mole ratio (more than 1:30 of FAL to ethanol) and high cost of catalyst are the major drawback. With our catalyst we have obtained 96% yield of EL within 2 h and with 1:15 mole ratio of ethanol and at 120°C. The results shows that prepared catalyst is better than different reported heterogeneous catalyst in terms of activity and selectivity of EL.

#### **Optimization of reaction Parameters**

Different parameters affecting the reaction were studied and optimized for the highest possible yield under the specified condition and are explained in detail.

Effect of Speed of agitation

Agitation speed effect was studied (200 to 1000 rpm) to witness that beyond 800 rpm, there was no effect on conversion and yield (supplementary Figure S1). To be on safer side we have chosen 900 rpm for the further study.



**Fig. 10**Effect of various catalysts on yield of EL. Furfuryl alcohol 0.048mol, Ethanol 0.72 mol, catalyst loading 7.5 g/L, temperature 120°C, speed of agitation 800rpm, total volume 0.041 L and reaction time 120 min.

#### Effect of catalyst loading

In the absence of both mass-transfer and intra-particle resistances, increase in number of catalytic sites should always result in a proportional increase in initial reaction rate. Thus, the catalyst loading was changed from 2.5 to 10 g/L (Figure 11). The yield of EL was also increased with increase in catalyst loading. However, an increase in the loading beyond 7.5 g/L does not affect the overall yield of the EL as the minimum sites needed for the reaction were provided. So the 7.5 g/L was selected as optimum loading for subsequent studies.

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View Article Online Table 3: Summary of the catalytic results obtained for the synthesis of ethyl levilunate (EL) from levelinite acide (ICA2466A and furfuryl alcohol (FAL) with ethanol over heterogeneous catalysts reported in literature

S. No.	Substrate	Catalyst	Mole ratio	T (°C)	X <sub>R</sub> (%)	Y <sub>EL</sub> (%)	t (h)	Ref.
	(R)		(R: EtOH)					
1.	LA	$SO_4/SnO_2$	1:5	70	44	44	5	35
2.	LA	Amberlyst-15	1:5	70	54	54	5	35
3.	LA	40WD/S	1:64	78	76	76	10	36
4.	LA	H/BEA	1:6	78	40	40	5	37
5.	LA	UDCaT-5	1:20	160	98	98	3	16
6.	LA	Zr-MOFs	1:15	78	94	94	8	38
7.	FAL	HPA-ZrO <sub>2</sub>	1:51	120	100	48	6	39
8.	FAL	SO4 <sup>2-</sup> /ZrO <sub>2</sub>	1:30	200	n.g	64.3	2.5	40
9.	FAL	SO4 <sup>2-</sup> /TiO <sub>2</sub>	1:30	200	n.g.	68.3	2.5	40
10	FAL	HZ-5	1:6	140	100	73	4	41
11	FAL	ZSM-5	1:51	120	100	85.8	6	39
12.	FAL	Al-TUD-1	1:57	140	100	80	24	42
13.	FAL	GO	1:51	120	100	95.5	6	39
14.	FAL	Amberlyst-15	1:57	90	140	90	4	42
15.	FAL	SO <sub>3</sub> H/AC	1:51	120	100	89.6	6	39
16.	FAL	[BMIm-SH] [HSO <sub>4</sub> ] IL	~1:40	130	99	94	2	43
17.	FAL	(HSO <sub>3</sub> -p) <sub>2</sub> im]- [HSO <sub>4</sub> ] IL	1:34	110	100	95	3	6
18.	FAL	1M-SZF	1:15	120	100	96	2	This work

n.g.=not given

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**Fig 11:**Effect of catalyst loading on (a) conversion of furfuryl alcohol (FAL) and (b) yield of Ethyl levulinate (EL). Furfuryl alcohol 0.048mol, ethanol 0.72 mol, temperature 120°C, speed of agitation 900rpm, total volume 0.041 L.

(◇) 2.5 g/L, (■) 5 g/L, (△) 7.5 g/L, (<sub>×</sub>) 10 g/L

#### Effect of the mole ratio

The moles of the ethanol with respect to FAL were varied in such a way that the total volume remained constant and hence the loading and other parameters remained the same (Figure 12). The mole ratio of FAL to Ethanol was varied from 1:05 to 1:20 under the same reaction condition. The change in mole ratio of ethanol with FAL enhances the rate of formation of EL as it is changed from 1:05 to 1:15 beyond which no distinct change in the rate and overall yield of the

EL was noticed. Lower mole ratio between FAL to ethanol results in polymerization of furfuryl arcohol in the presence of strong acidic catalyst. It confirmed that the optimum mole ratio of FAL to EL is 1:15 to get maximum yield of EL under the specified reaction condition.



**Fig. 12:** Effect of mole ratio of FAL to ethanol on (a) conversion of furfuryl alcohol (FAL) and (b) yield of ethyl levulinate (EL). Catalyst loading 7.5 g/L, temperature 120°C, speed of agitation 900rpm, total volume 0.041 L.( $\diamondsuit$ ) 1:05, (

#### ) 1:10, (△) 1:15, (<sub>×</sub>)1:20

#### Effect of temperature

Under optimized reaction conditions (catalystloading 7.5 g/L, mole ratio of furfuryl alcohol to ethanol 1:15 and speed 900 rpm), reaction temperature was varied from 100 to 130°C (Figure 13). In all cases the conversion of FAL is 100%, but the conversion of intermediates to final product ethyl levulinate is greatly dependent on the temperature. It also confirms that the rate limiting stepis not the conversion of

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FAL to intermediate (ethoxymethylfuran) but conversion of intermediate to EL. The rate of formation of EL increases with increase in temperature, but after 120°C there is no basic difference in yield of EL after 2 h. Hence 120°C was considered as optimum reaction temperature.



**Fig. 13**Effect of temperature on (a) conversion of furfuryl alcohol (FAL) and (b) yield of ethyl levulinate (EL). Furfuryl alcohol 0.048mol, ethanol 0.72 mol, catalyst loading 7.5 g/L, speed of agitation 900rpm, total volume 0.041 L.( $\diamond$ ) 100°C,

#### ( $\blacksquare$ ) 110°C, ( $\triangle$ ) 120°C, ( $_{\times}$ )130°C

#### Catalyst reusability studies

The magnetically separable catalyst was separated using external magnet, dried for 4 h at 120 °C and used again. No regeneration was done. Makeup of fresh catalyst was done for any loss. The yield of EL found to be decrease significantly from 96% to 56% after 2 h. It may be due to the blockage of pores or active sites caused by the different

## adsorbed products. Hence the additional regeneration method was employed. The recovered catalyst was further calcined at 500°C in order to get rid of any adsorbed material on the surface. The same procedure was followed each time after the reaction and catalyst reused for 8 times. The recovered catalyst was made by approximately 5% (by weight) to the original loading before the reaction. The reaction shows a decrease in yield of ethyl levulinate from 96% to 92% after first reuse which further decreases to 89% (second reuse) and remains consistent as it gives 88.1% and 87.8% yield of EL after 4<sup>th</sup> and 8<sup>th</sup> reuse, respectively. This decrease in conversion can be correlated to decrease in acidity (Table 2, entry 8, 9 and 10). Acidity of catalyst decreases significantly up to 2<sup>nd</sup> reuse and remains almost constant for further cycles. The decrease in acidity is may be due to leaching of some active sulfate ions. The reused catalyst was further characterized by XRD, FTIR, ASAP and NH<sub>3</sub>-TPD. The basic structure and morphology of catalyst was found to be the same as shown in characterization and the acidity possessed by the catalyst was slightly changed.

#### Leaching test of the catalyst

In the literature it is reported that the sulfate ions tend to leach in the reaction medium and hence catalysed the system homogeneously.<sup>17-19</sup> Also, in reusability test we have seen a decrease in acidity which may be due to the leaching of some active sulfate ions. To confirm the heterogeneous nature and the stability of prepared catalyst, hot filtration method was used. The reaction was stopped after 40 min as at this point all FAL is converted to the intermediate along with a little EL. The catalyst was separated using a magnet and the clear reaction mass was again placed in the reaction vessel. The reaction was further continued for next 2 h at 120°C. After 2 h reaction mixture was analysed and it was found that there was no further conversion of the intermediates. This confirms that there is no leaching of the active sulfate ion in the reaction mass or the amount of sulfate ions are very low and hence it does not results in significant change in conversion.

#### Reaction mechanism and kinetic model

Apart from EMF none of the intermediates were observed experimentally. Overall mechanism is based on the reported literature.<sup>11, 15</sup>

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Scheme2. Proposed mechanism for the formation of ethyl levulinate from furfuryl alcohol

The most feasible path is the formation of alkoxy furfuryl alcohol and its further conversion to the alkoxylevulinate in the presence of water. <sup>15</sup>Here we have used ethanol as a source of alcohol. The concentration profiles at optimized condition (Figure 14 and ESI Figure S2) of the analysis implies that first there is a formation of intermediate (identified as EMF by using GC-MS ) which is the fast step as compared to the second step of formation of the ethyl levulinate from the EMF (Scheme 1). The possible mechanism of formation of the EL is shown in Scheme 2 based on the earlier reports.<sup>6, 8, 11, 14</sup>FAL reacts with ethanol to form the intermediate EMF (i), which is then converted to another intermediate (ii). Further, it protonates to give cyclic oxonium (iii). The electron pair transfer in cyclic oxonium yields exocyclic oxonium compound (iv). The exocyclic oxonium then undergoes the ring opening reaction in the presence of water to form the intermediate species (v) which isomerizes to give the desired product ethyl levulinate (vi). From the above mechanism, it is clear that water is required for the formation of final product EL.

To confirm it, the two different sets of the experiment were performed. Firstly, the reaction was conducted under optimized conditions and stopped it after 40 min because at this time the total FAL was converted into the intermediate along with the EL (about 48 % yield). The catalyst was filtered out and fresh catalyst was added in order to get rid of the water adsorbed on the surface of catalyst. Further dried molecular sieve was added to absorb the water present in the reaction mixture and started the reaction again. In second experiment, to see the effect of water on the rate, different moles of water were added in the system. In each experiment the above method was repeated as the initial addition of water may result in formation of levulinic acid in the acidic condition. In first experiment one equivalent water (approximately equivalent to the moles of EMF remaining after 40 min i.e. 0.025 mol) was added and started reaction. In second experiment, two equivalent of water (i.e.0.05 mol)

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and in the third 4 equivalent of water (i.e.0.1 mol) were added.



Fig. 14 Concentration profiles of different products with time. Furfuryl alcohol 0.048mol, Ethanol 0.72 mol, catalyst loading 7.5 g/L, temperature 120°C, speed of agitation 900rpm, total volume 0.041L.



**Fig. 15:**Influence of the water content on the yield of ethyl levulinate after 40min. Furfuryl alcohol 0.048mol, ethanol 0.72 mol, water (set amount) catalyst loading 7.5 g/L, Speed of agitation 900 rpm, temperature 120°C, total volume 0.041 L.

( $\clubsuit$ ) Without water, ( $\clubsuit$ ) with 1 equivalent water, ( $\clubsuit$ ) with 2 equivalent water, ( $\bigstar$ ) with 4 equivalent water.

The results are shown in the Figure 15. The rate of formation of EL got affected by the removal of water and it gave only 60% yield in 2 h as compared to 98% with 1 equivalent water. The increase in yield of EL even after removal of water is due to the presence of trace of water which could not be removed by above mentioned procedures. Further the addition of water greatly enhances the formation of EL from the 48% to almost 100% within 120 min for 2 equivalents of water while it reached to 98% with one equivalent of water within 2 h. The addition of EL. Hence, from this study, it is clear that the water formed in the system is responsible for the formation of EL from the intermediate as reported earlier in the formation of butyl levulinate.<sup>14</sup>

With above discussion, we further developed a mathematical model for reaction. As shown in Scheme 2, formation of EL from FAL is achieved through various steps. However, all the intermediates have not been detected. Hence we can summarize that overall reaction in terms of single intermediate formed (i.e. EMF) is shown in Scheme 1. Initial analysis showed that all species are weakly adsorbed.

Consider A (FAL), B (Ethanol), C (EMF), D (EL) and W (water).

The adsorption of FAL and ethanol to the catalytic surface S is given by:

$$A + S \xrightarrow{\kappa_A} AS \tag{0}$$

 $B + S \xrightarrow{K_B} BS \tag{2}$ 

The surface reaction of adsorbed species AS and BS gives the intermediate CS as

$$AS + BS \square \square CS + WS$$

1

Further the reaction between CS and WS gives the desired product DS

$$CS + WS \square \bigoplus_{k_2}^{k_2} DS + S$$
<sup>(4)</sup>

The desorption step of different products can be written as:

$$CS \xrightarrow{\frac{1}{K_c}} C + S \tag{5}$$

$$DS \xrightarrow{\overline{K_D}} D + S$$
 (6)

As discussed above the conversion of intermediate to the EL is slow. Therefore considering it as a rate determining step,

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Table 4	Kinetic parameters evaluation of the reaction

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Sr. No	T (°C)	$k_1 X 10^4$ ( $L^2 mol^{-1}g^{-1}s^{-1}$ )	$k_2 X 10^4$ (L <sup>2</sup> mol <sup>-1</sup> g <sup>-1</sup> s <sup>-1</sup> )	$k_1^{'} \times 10^4$ (L <sup>2</sup> mol <sup>-1</sup> g <sup>-1</sup> s <sup>-1</sup> )	$k_{2 \ X10^{4}}^{'}$ (L <sup>2</sup> mol <sup>-1</sup> g <sup>-1</sup> s <sup>-1</sup> )
1.	100	1.9	0.1	0.005	0.0006
2.	110	3.36	0.19	0.012	0.0021
3.	120	5.14	0.36	0.022	0.0072
4.	130	7.1	0.63	0.040	0.016

all other steps will be in equilibrium and the intermediates concentration can be written as:

$$C_{AS} = K_A C_A C_S \tag{7a}$$

$$C_{BS} = K_B C_B C_S \tag{7b}$$

$$C_{CS} = \frac{k_1 C_{AS} C_{BS}}{k'_1 C_{WS}}$$
(7c)

The rate equation for the two steps can be written as can be written as:

$$r_{1} = k_{1}C_{AS}C_{BS} - k_{1}C_{CS}C_{WS}$$

$$r_{1} = k_{1}K_{A}C_{A}K_{B}C_{B}C_{S}^{2} - k_{1}K_{C}C_{C}K_{W}C_{W}C_{S}^{2} \qquad (8)$$

$$r_{2} = k_{2}C_{CS}C_{WS} - k_{2}C_{DS}C_{S}$$

$$r_{2} = k_{2}K_{C}C_{C}K_{W}C_{W}C_{S}^{2} - k_{2}K_{D}C_{D}C_{S}^{2} \qquad (9)$$
The total activities give below on the given as

The total catalytic site balance can be given as

$$C_T = C_{AS} + C_{BS} + C_{CS} + C_{WS} + C_S$$
(10)

From the above equations, we have

$$C_{S} = \frac{C_{T}}{1 + K_{A}C_{A} + K_{B}C_{B} + K_{C}C_{C} + K_{D}C_{D} + K_{W}C_{W}}$$
(11)

From equation 8,9, 10 and 11 we have,

$$r_{1} = \frac{\left[k_{1}K_{A}C_{A}K_{B}C_{B} - k_{1}K_{C}C_{C}K_{W}C_{W}\right]w}{1 + K_{A}C_{A} + K_{B}C_{B} + K_{C}C_{C} + K_{D}C_{D} + K_{W}C_{W}}$$
(12)

$$r_{2} = \frac{\left[k_{2}K_{C}C_{C}K_{W}C_{W} - k_{2}K_{D}C_{D}\right]w}{1 + K_{A}C_{A} + K_{B}C_{B} + K_{C}C_{C} + K_{D}C_{D} + K_{W}C_{W}}$$
(13)

Using above equation we have calculated the different constants for the reaction. The values of the adsorption constants were found to be very small hence the above equation can be reduce to:

$$r_{1} = \left[ k_{12}C_{A}C_{B} - k_{12}C_{C}C_{W} \right] W$$
(14)

$$r_{2} = \left[k_{22}C_{C}C_{W} - k_{22}C_{D}\right]W$$
(15)

Where,

$$k_{12} = k_1 K_A K_B, k_{12} = k_1 K_C K_W, k_{22} = k_2 K_C K_W, k_{22} = k_2 K_C K_W$$

Different rate constants were evaluated and listed in Table 3.We can see that rate constant value of first step, i.e. formation of ethoxy methyl furfural is greater than that for the second step. Hence the first step is fast as compared to second step. Also, we can see the values of backward rate constants are very small as compared to the forward reaction. Hence we can conclude that reaction is irreversible. The Arrhenius plots for different steps were plotted (ESI, Figure S3, S4) to calculate activation energy. The activation energy values for step 1 and step 2 were found to 13.1 kcal/mol, 18.4 kcal/mol for forward reactions, respectively. The values of the energy confirm that the reaction is kinetically controlled.

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#### Conclusion

We have successfully synthesized magnetically separable sulfated zirconia catalysts and compared their activity for synthesis of ethyl levulinate from furfuryl alcohol and ethanol. 1M-SZF possesses the highest acidity and activity as it gives 96% yield of EL with 100% conversion of FAL with 1:15 mole ratio in 2 h. The use of magnetic particles in the synthesis of catalyst helps to get the high amount of acidity apart from its easy separation. The catalyst is separated by using magnetic field and is recycled for 8 times and found to be active. The detail study was carried out to optimize the reaction conditions to get an optimum yield of ethyl levulinate. A kinetic model was developed and two different rate constants were calculated. The activation energy values for different steps confirm that reaction is kinetically controlled. The overall process is clean and green.

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#### **Conflict of Interest Statement**

The authors declare no conflict of interest.

#### Nomenclature

- A reactant species A, Furfuryl alcohol(FAL)
- B reactant species B, Ethanol
- C Ethoxymethylfuran (EMF)
- D Ethyl levulinate (EL)
- $C_A$  concentration of A, (mol/L)
- $C_B \qquad \text{concentration of } B, \, (\text{mol}/\text{L})$
- $C_C \qquad \text{concentration of } C \text{ in, ( mol/L)}$
- $C_D$  concentration of D in, (mol/L)
- $C_W$  concentration of W in, (mol/L)
- $k \qquad \mbox{reaction rate constant } (L^2 mol^{-1}g^{-1}s^{-1})$

- K adsorption equilibrium constant for  $(\underline{I}_{MeWArticle}^{-1})_{NeWArticle}$  online M mala ratio of A to B DOI: 10.1039/C6GC02466A
- M mole ratio of A to B
- r rate of surface reaction (mol  $L^{-1}s^{-1}$ )
- W water
- w catalyst loading(g/L)
- X<sub>A</sub> fractional conversion of A

#### Acronyms

UDCaT-5	University	Department	of	Chemical	Technology
	catalyst -5				

- FLSZ Fuel lean sulfated zirconia
- F Magnetic Particles ( $Fe_3O_4$ )
- ZrOH<sub>4</sub>-F ZrOH<sub>4</sub> Coated magnetic particles
- ZF ZrO<sub>2</sub> Coated magnetic particlesSZF Magnetically separable sulfated zirconia

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# **GRAPHICAL ABSTRACT**

# Magnetically separable sulfated zirconia as highly active acidic catalyst for selective synthesis of ethyl levulinate from furfuryl alcohol

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