

Esterification of levulinic acid with alcohol catalyzed by hierarchically porous ZSM-5 zeolites: A study on catalyst efficiency and product selectivity

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This study evaluates the catalytic performance of ZSM-5 zeolites synthesized using corn stem pith powder as a hard template in the esterification of levulinic acid with 1-propanol and heptanol. The structural and textural properties of the zeolites have been characterized, revealing a hierarchical porous nature. The catalytic activity of the ZSM-5 is assessed in the esterification of levulinic acid with 1-propanol and heptanol, yielding corresponding esters with high selectivity. The effects of reaction parameters, including temperature, molar ratio, catalyst loading, and reaction time, are systematically studied to optimize reaction conditions. The reusability and stability of the catalyst are evaluated through multiple reaction cycles. The results are compared with those obtained using conventional ZSM-5, highlighting the advantages of the meso porous structure. This study provides valuable insights into the design of hierarchical zeolite catalysts for green and sustainable chemistry applications. The use of corn stem pith powder as a hard template enhances the textural properties of the zeolite while promoting sustainability and resource efficiency.

Keywords: ZSM-5 Zeolites, Levulinic ester, Catalytic activity, IR, NMR

Levulinic acid (LA), a key platform chemical derived from biomass, holds significant promise as a precursor for the production of a wide range of value-added chemicals and bio fuel^{1,2}. Among the various derivatives of levulinic acid, levulinate ester³⁻⁶ stands out due to its versatile applications as a green solvent, fuel additive, and intermediate for the synthesis of fine chemicals and pharmaceutical⁷. The production of levulinate ester is commonly achieved through the esterification of levulinic acid with ethanol, propanol, *etc.* in the presence of an acid catalyst. Developing an efficient, sustainable, and environmentally benign catalytic system for this reaction is critical for the advancement of biomass valorization technologies⁸⁻¹⁴.

Zeolites, particularly ZSM-5, have garnered considerable attention as catalysts due to their unique structural features, including well-defined microporosity, high thermal stability, and tunable acidity. Their catalytic performance can be further enhanced by modifying their textural properties, such as introducing meso porosity. The incorporation of meso

porosity into ZSM-5 allows for improved mass transfer, which is especially beneficial for reactions involving bulky molecules¹⁵⁻¹⁷. Moreover, the creation of hierarchical pore structures can enhance the accessibility of active sites, thus boosting catalytic activity. In this context, micro-meso-meso porous nature of ZSM-5 zeolites presents an attractive option for the esterification of levulinic acid to levulinate ester¹⁸. The preparation of micro-meso-meso porous ZSM-5 zeolites typically involves the use of hard or soft templates to introduce mesoporosity¹⁸⁻²⁰. Hard templates, such as biomass-derived materials, are particularly appealing due to their sustainability, low cost, and availability²¹⁻²⁷. Among the various biomass-derived templates, corn stem pith powder stands out as an effective hard template due to its porous structure, high surface area, and renewable nature. The use of corn stem pith powder not only aligns with the principles of green chemistry but also offers an opportunity for the valorization of agricultural waste. The selection of this catalyst is motivated by its

potential to address the limitations of conventional ZSM-5, such as restricted diffusion and limited accessibility of active sites. By utilizing corn stem pith powder, the synthesized hierarchically porous ZSM-5 zeolites exhibit enhanced textural properties, including larger pore size, increased pore volume, and improved acid site accessibility. The introduction of mesoporosity into ZSM-5 *via* biomass-derived templates is a promising strategy for enhancing the catalytic performance of zeolites. The corn stem pith powder serves as a sacrificial template, creating mesopores upon its removal during the synthesis process. The resultant hierarchical structure combines the advantages of both micropores and mesopores, facilitating efficient diffusion of reactants and products while maintaining strong acidity for catalytic activity. Furthermore, the use of a biomass-based template contributes to the sustainability of the catalyst preparation process. Esterification is a fundamental reaction in organic synthesis and is widely employed in industrial processes for the production of esters. In the context of levulinic acid valorization, the esterification reaction represents a key step toward the production of bio-fuels and renewable chemicals. ZSM-5 zeolite with hierarchical porous nature represents a robust class of heterogeneous acid catalysts, combining strong acidity with enhanced mass transfer properties.

In this work, ZSM-5 zeolites synthesized using corn stem pith powder as a hard template are evaluated for their catalytic performance in the esterification of levulinic acid with 1-propanol and Heptanol. The structural and textural properties of the synthesized zeolites are thoroughly characterized using various techniques and reported elsewhere²⁷. The catalytic activity of the ZSM-5 with hierarchical porous nature of the zeolites is assessed in esterification of levulinic acid with 1-propanol and Heptanol to corresponding ester yield, and selectivity. The effects of reaction parameters, including reaction temperature, propanol-to-levulinic acid molar ratio, catalyst loading, and reaction time, are systematically studied to optimize the reaction conditions. Additionally, the reusability and stability of the catalyst are evaluated through multiple reaction cycles. The results are compared with those obtained using conventional ZSM-5 to highlight the advantages of the mesoporous structure. The findings of this study are expected to provide valuable insights into the design of hierarchical zeolite catalysts for green

and sustainable chemistry applications. The use of corn stem pith powder as a hard template not only enhances the textural properties of the zeolite but also aligns with the principles of sustainability and resource efficiency.

Results and Discussion

Characterization of ZSM-5 catalysts

The synthesized ZSM-5 catalysts were characterized by various techniques and reported in our previous work. The powder XRD patterns of prepared are exhibited the characteristic Bragg reflections corresponding to MFI framework types, which confirmed the formation of zeolites²⁷. Nitrogen adsorption and desorption isotherms of the prepared corn ZSM-5 have hysteresis at $p/p_0 \approx 0.2$, a second hysteresis, observed above $p/p_0 \approx 0.4$, in Corn-ZSM-5 indicates the formation of additional porosity with hierarchical micro-mesopores. The broadness and shape of this isotherm reveal that cage like type of pores is present in addition to intrinsic micropores of zeolites²⁷. The TEM images show the typical coffin-shaped morphology of MFI zeolite. This observation is in good agreement with nitrogen adsorption and pore size distribution. Temperature programmed desorption of ammonia (NH₃-TPD) was performed to analyse acidic sites of prepared zeolites. The position and area of the peaks in the TPD of ammonia traces can be correlated to acidity distribution of zeolites. The Al MAS NMR spectra of the prepared zeolites exhibited. The first resonance peak was found at 57 ppm which can be correlated to framework Al in tetrahedral coordination²⁷. The second, small resonance appeared at 4 ppm is related to Al in octahedral coordination in zeolite framework. These observations indicate that almost all of the aluminum ions are incorporated in tetrahedral framework of zeolites²⁶. But the conventional ZSM-5 zeolites does not show hierarchically porosity²⁷. In our previous work, we have studied the corn ZSM-5 catalyst showed enhanced catalytic activity in benzylolation of mesitylene²⁷.

Esterification of Levulinic Acid

The prepared materials were tested as solid acid catalysts in esterification of levulinic acid (LA) with 1-propanol and 1-heptanol under optimized reaction conditions. Levulinic acid is a platform chemical obtained from biomass which can be converted into

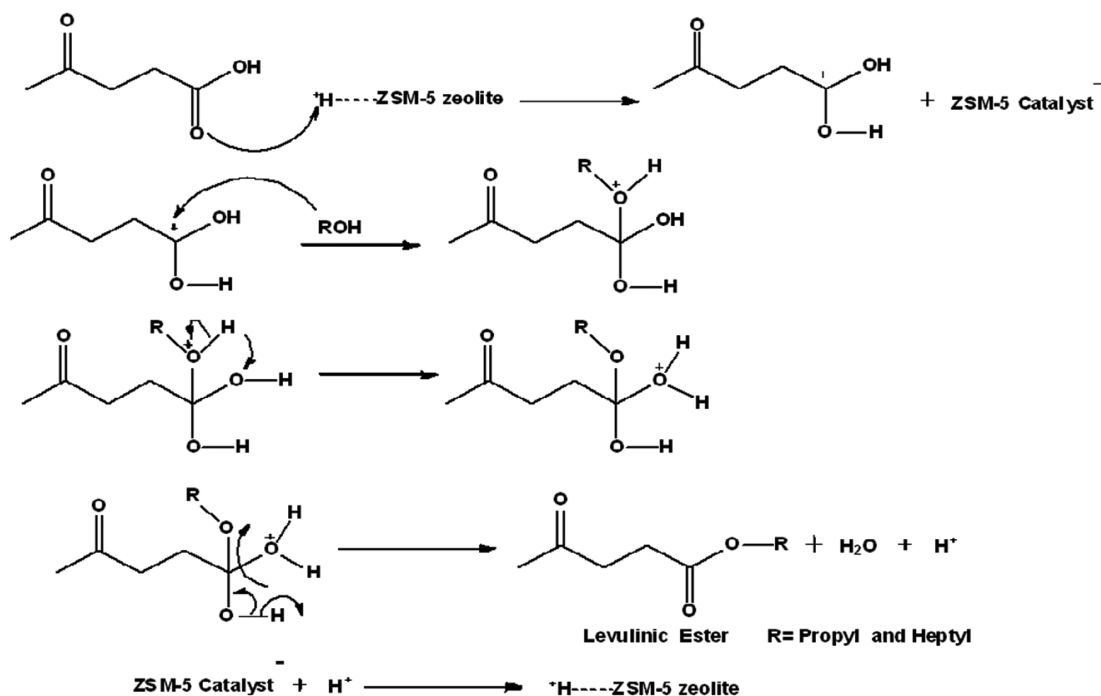
variety of value-added chemicals and fuel additives²⁷. Esterification of renewable levulinic acid with alcohol is a reaction that could be used to produce corresponding levulinate ester products which are useful as fuel additives, lubricants and perfume and flavoring chemicals²⁷. In the reaction of LA with ethanol, found that the conversion of LA increased from 30% on conventionally prepared ZSM-5 zeolite to 80% on ZSM-5 possessing micro/meso hierarchical structure. The esterification of LA may occur to a small extent even in the absence of a catalyst, because LA is able to auto catalytically facilitate the reaction. For this reason, a reaction was also carried out in the absence of catalyst. The results of the catalytic activity studies are shown in Table 1. In all the reactions, LA to alcohol ratio was maintained as 1:5 to facilitate the forward reaction. In the absence of catalyst, the observed conversions of LA were 12 and 13% for 1-propanol and 1-heptanol respectively. The table shows the

conversion rates of levulinic acid with 1-propanol and 1-heptanol, with and without catalysts. Without a catalyst, the conversion rates were: 15% with 1-propanol (20% selectivity) and 25% with 1-heptanol (35% selectivity) when we test using a conventional ZSM-5 catalyst, the conversion rates improved to: 25% with 1-propanol (38% selectivity) and 32% with 1-heptanol (30% selectivity) However, using the Corn ZSM-5 catalyst synthesized from corn stem pith powder, the conversion rates were significantly higher: 75% with 1-propanol (99% selectivity) and 90% with 1-heptanol (99% selectivity) which clearly indicated the presence of hierarchical pores in ZSM-5 zeolites and also correlated with nitrogen adsorption and desorption techniques. In addition, the improved catalytic activity shows, the prepared materials exhibited the acidity and all Al present in tetrahedral site. The proposed general mechanism of esterification was illustrated in Scheme 1.

Table 1 — Conversion of levulinic acid with 1-propanol and 1-heptanol over different catalysts

Alcohol→ Catalyst↓	Yield (%)	
	1-Propanol	1-Heptanol
Without catalyst	15 (20)	25(35)
Conv ZSM-5	25 (38)	32 (30)
Corn ZSM	75 (99)	90 (99)

Values given in the parenthesis indicate selectivity of the corresponding ester products. Reaction conditions: Temperature = 100°C; 1-Propanol: LA Mole ratio = 5:1, Catalyst weight = 100 mg; Time = 5 h



Scheme 1 — Proposed general reaction mechanism of formation of levulinate ester

The enhancement in catalytic activity of the zeolites prepared using corn stem pith powder is in good agreement with the physicochemical characterization results discussed above. The results indicate that hierarchical pores are introduced on to the zeolites when corn stem pith powder was added to the synthesis gel. The fact that conversion of LA increases with increasing the quantity of corn stem pith powder added to the zeolite synthesis gel indicate that hierarchical pores are responsible for the enhancement in the catalytic activity. We presume that the hierarchical pores help to overcome diffusion limitations experienced by the reactants and products causing the enhanced catalytic activity.

Influence of Temperature, Time and Catalyst Weight

The effect of temperature, reaction time and catalyst weight were tested using esterification of LA with 1-propanol using Corn ZSM (500) as an example. The conversion of LA improved while increasing the reaction temperature from 30 - 100°C and the maximum LA conversion was observed at 100°C as shown in Fig. 1. The reaction was conducted for 1, 2, 3, 5 and 6 h to see the effect of time on LA conversion shown in Fig. 2. The conversion found to increase from 1 to 5 h and reach the maximum of 80%. The further increase in time did not influence the conversion.

The effect of the Corn ZSM weight on the LA conversions was tested and it can be seen from Fig. 3. The increase in catalyst weight leads to improvement in LA conversion as it will increase the number of acid sites available for catalysis. Above 100 mg of the added catalyst, not much improvement in LA conversion noticed. In all the reactions studied, the selectivity of the ester product was found to be 98-99%.

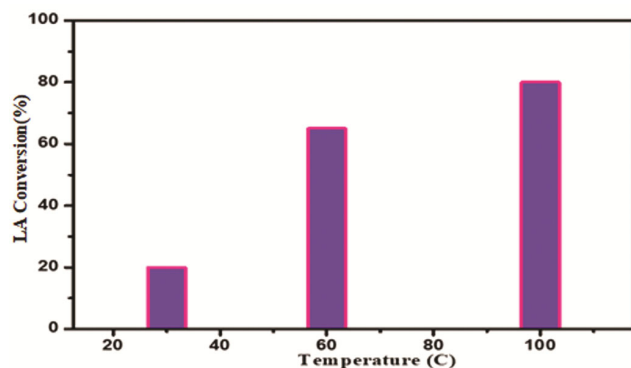


Fig. 1 — Effect of Temperature on levulinic acid conversion (Catalyst = Corn ZSM, 100 mg, 1-propanol)

Reusability of Catalyst

The recycling ability of the catalysts were investigated under the optimized experimental conditions as shown in Fig. 4. After completion of each recycle, the catalysts were filtered washed with

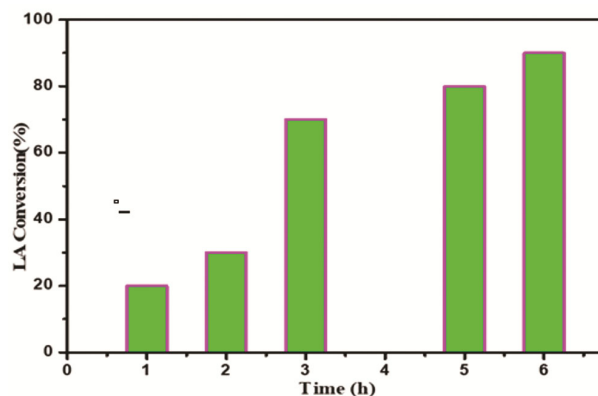


Fig. 2 — Effect of time on levulinic acid conversion (Catalyst = Corn ZSM, 100 mg, Temperature =100°C, 1-propanol: LA mole ratio = 5:1). anol:LA mole ratio = 5:1, time= 5 h)

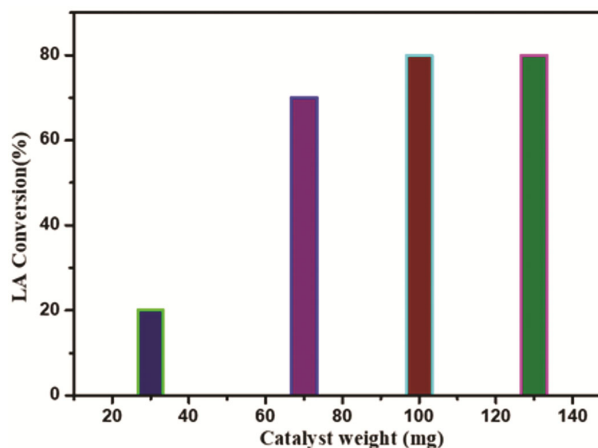
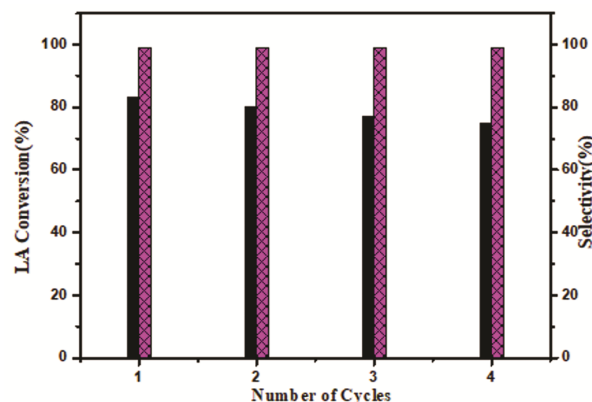


Fig. 3 — Effect of weight on levulinic acid conversion (Catalyst = Corn ZSM, Temperature =100°C, 1-Propanol: LA mole ratio = 5:1, time= 5 h)



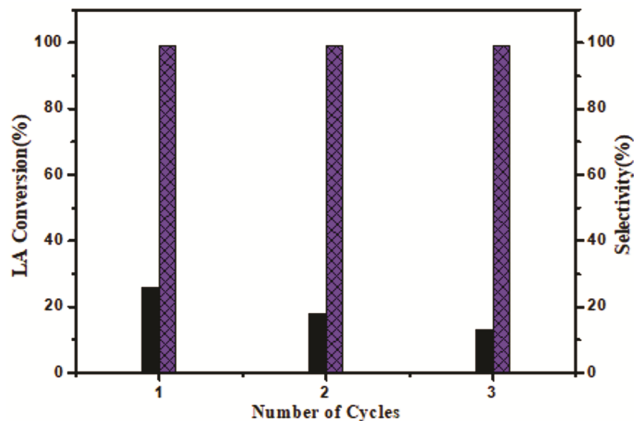
Reaction Conditions: LA:propanol ratio 1:5, 100 mg catalyst, Time 5 h, Temp. 100°C

Fig. 4 — Recycling of CZSM

1-propanol, dried in hot air oven at 80°C and then used for next cycle. Even after four repeated use, the conversion of LA in 1-propanol is found to remain almost the same for Corn ZSM showing the stable nature of these catalysts. In the case of Conv ZSM the catalytic activity was found to decline over the recycles Fig. 5 and Fig. 6 shows the recyclability nature of of Corn ZSM-5 zeolites for 1-heptanol and the results shows remain 100%. The presence of only micropores in these catalysts and resulted diffusion limitations caused by the coke formed or accumulation of bulky side products in the reactions may make them less reactive during the recycles.

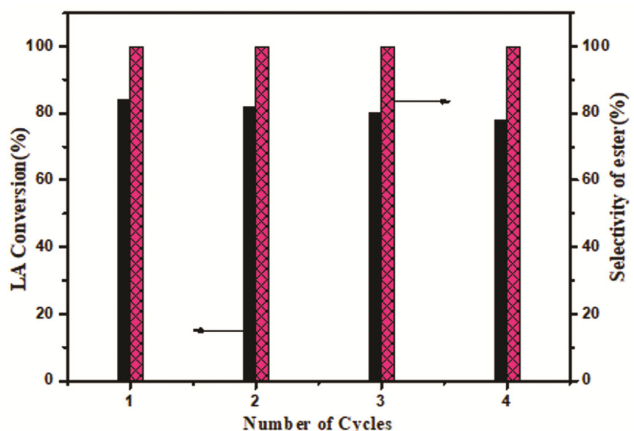
NMR spectral study of levulinate ester

The levulinate ester was separated and confirmed the formation of product by NMR. The results were given in Fig. 7. The Fig. 7 shows the ^1H NMR spectrum of Propyl Levulinate, with peaks at 3.937–3.954 ppm corresponding to the OCH_2 protons in the ethoxy group, 2.101–2.684 ppm representing the $\text{CH}_2\text{-COO}$ and $\text{CH}_2\text{-CO}$ protons adjacent to the ester and ketone groups, 1.528–1.580 ppm matching the CH_2 protons in the propyl chain, and 0.827–0.864 ppm aligning with the CH_3 protons at the end of the propyl chain. However, the peak at 7.282 ppm is not expected for Propyl Levulinate and likely indicates the presence of an aromatic impurity, such as residual solvent (e.g., CHCl_3 in CDCl_3) or an aromatic



Reaction Conditions: LA:propanol ratio 1:5, 100 mg catalyst, Time 5 h, Temp. 100°C

Fig. 5 — Recycling of Conv ZSM



Reaction Conditions: LA:1-Heptanol ratio 1:5, 100 mg catalyst, Time 5 h, Temp. 100°C

Fig. 6 — Recycling of CZSM

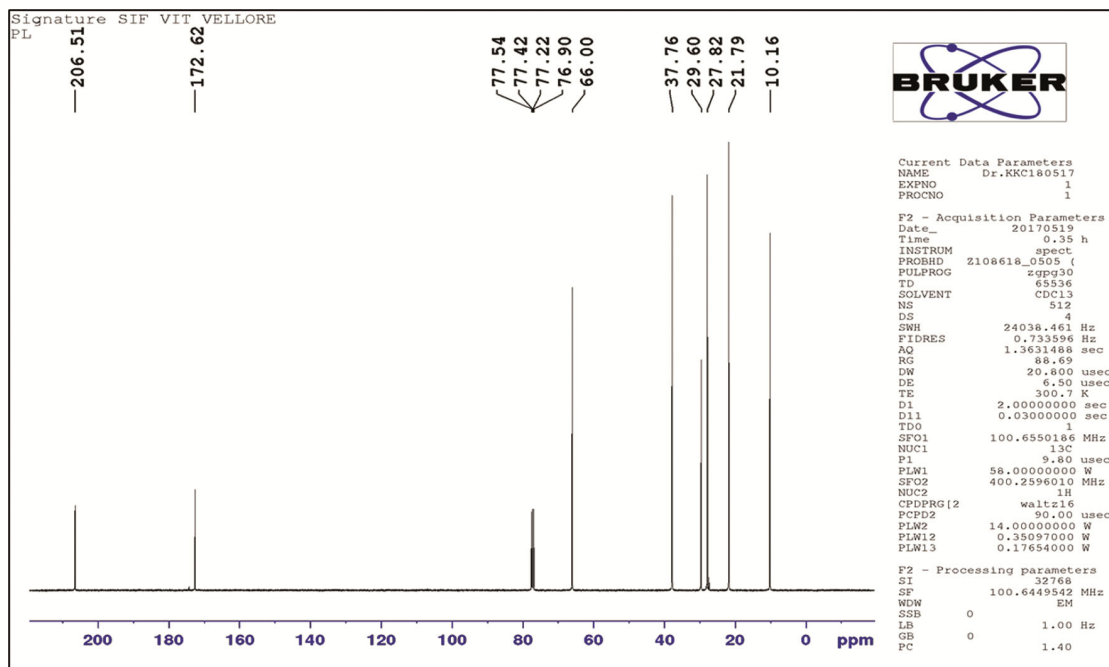


Fig. 7 — ^1H NMR spectra of Propyl Levulinate

byproduct. This peak should be investigated further to ensure the purity of the sample. Overall, the chemical shifts provide a clear fingerprint of Propyl Levulinate, with the exception of the aromatic signal. Propyl Levulinate does not have aromatic protons, peak around 7.2 ppm is likely due to an impurity or residual solvent (*e.g.*, CHCl₃ in CDCl₃).

Fig. 8 shows the ¹³C NMR spectrum of Propyl Levulinate, the peak at 200.6 ppm corresponds to the carbonyl carbon of the ketone group (C=O), while the peak at 62.7 ppm matches the carbon attached to the oxygen in the ester group (OCH₂). The propyl chain carbons are observed at 22.9 ppm and 29.60 ppm, consistent with CH₂ groups, and the terminal CH₃ group appears at 17.2 ppm, slightly higher than expected but still plausible. Peaks at 37.76 ppm and 29.60 ppm likely represent carbons adjacent to the ketone group (CH₂-CO and CH₃-CO). However, peaks at 54.4 ppm, 66.0 ppm, 77.2 ppm, and 77.5 ppm are likely due to solvent (CDCl₃) or minor impurities, as they do not correspond to the expected shifts for Propyl Levulinate. Overall, the spectrum provides a clear fingerprint of the molecule, with minor deviations attributed to experimental conditions or impurities.

Experimental Section

Materials and Methods

Tetraethylorthosilicate (98%), fumed silica, tetraethylammonium hydroxide (40% in H₂O),

tetrapropylammonium hydroxide (40% in H₂O), sodium aluminate (Al₂O₃ = 50–56%), levulinic acid (98%), and poly (diallyldimethylammoniumchloride) (20 wt% in H₂O) were obtained from Sigma-Aldrich, India. Sodium hydroxide, 1-propanol (99%), and 1-heptanol (99%) were purchased from SD Fine Chemicals, India. All the chemicals obtained were used without further purification. Corn stems piths were collected from agricultural. The outer cover of the naturally dried stem pith of corn was removed and the spongy material present inside was cut into small pieces and made into fine powder using mortar and pestle after freezing it using liquid nitrogen.

Synthesis of Hierarchically porous ZSM-5 zeolite

Corn stem pith powder was added to 1% poly (diallyldimethylammonium chloride) (PDDA) solution and stirred for 2 h to modify the surface charge of corn stem pith powder. Then it was filtered and added into the zeolite precursor gel. In a typical synthesis, 1000 mg of PDDA modified corn stem pith powder was added to a mixture containing 7 g TEOS, 8 mL TPAOH, 2 g ethanol, 0.115 g sodium aluminate and 2 g distilled water and stirred for 2 h. The zeolite precursor gel molar ratio of was 30 SiO₂:7.3 TPAOH: 400 H₂O:5EtOH:xAl₂O₃ (Si/Al = 25). After stirring, the mixture was transferred to a Teflon lined containing the synthesis gel was kept in a hot

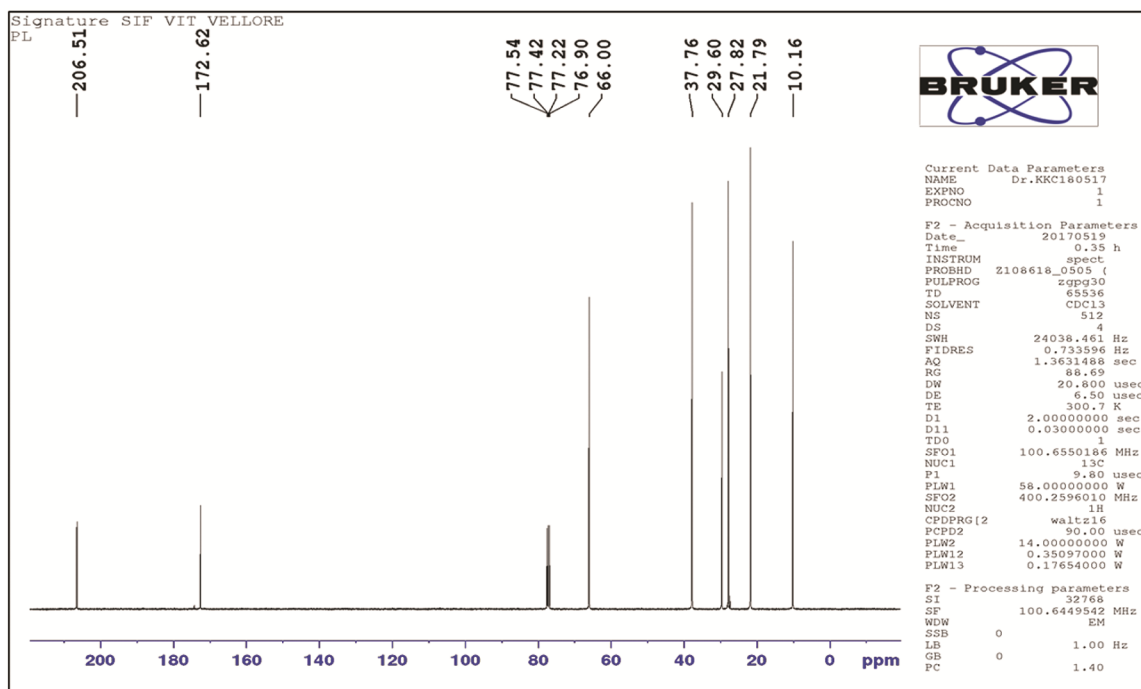
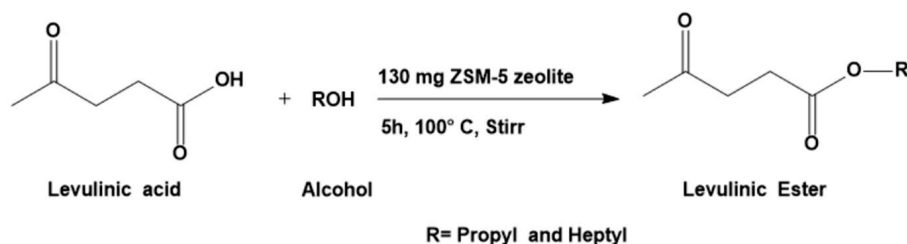


Fig. 8 — ¹³C NMR spectra of Propyl Levulinate



Scheme 2 — Esterification of levulinic acid with alcohols using ZSN-5 zeolite catalyst

air oven at 170°C for 36 h. After this autoclave. The tightly closed autoclave crystallization period, the autoclave was taken out from the hot air oven and quenched to RT. The solid in the autoclave was filtered, washed and dried in a hot air oven at 110 °C overnight and then calcined at 550°C under air to remove the templates. Finally, the Na form of ZSM-5 zeolite powder obtained was treated thrice with 1 M ammonium nitrate (NH₄NO₃) solution at 70°C for 5 h. The TPAOH/Si molar ratio zeolite gel was maintained at 0.25. The ion-exchange process was repeated thrice for complete ion exchange and then the material was thoroughly washed with distilled water. The ammonium form zeolite powder thus obtained was then dried at 80°C for 6 h and then calcined at 550°C for 5 h in air to get H⁺ form the zeolites. HZSM-5 zeolite without adding the corn stem pith was also prepared by following the above procedure and named as Conv ZSM.

General procedure for esterification

Quantitatively 1:5 ratio of levulinic acid, propanol/heptanol and 130 mg of prepared preactivated ZSM-5 zeolite catalyst were refluxed water bath for 5h with stirring (Scheme 2). The completion of the reaction was monitored using gas chromatograph (Shimadzu GC 2010 plus, RTX-1 capillary column, length 30 m, 0.32 mm ID, film thickness 0.5 μm) by internal standard method. N-Nonane was used as an internal standard. The reaction mixture after filtration of the catalyst was added into 15 mL dichloromethane followed by washing with 50 mL of water. The washing was repeated for three times. After washing, the contents were dried using MgSO₄ and then propyl levulinate was separated by evaporating the solvent using a rotary evaporator. Further the purities of the synthesized ester was confirmed by their physical constants.

Conclusion

Hierarchically porous ZSM-5 Zeolite was prepared by agricultural wastes materials, corn stem pith powder as a secondary pore inducing agent. The hierarchical solid acid catalyst thus prepared is useful for the conversion of biomass derived levulinic acid into value added ester as they showed enhanced catalytic activity. The presence of secondary pores improves mass transfer within the zeolites. The hierarchically zeolite prepared exhibit sustainable catalytic activity even after four consecutive recycles in esterification of levulinic acid.

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