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Efficient 5-HMF production from Glucose and Fructose by using solid acid super catalyst

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Abstract:
The glucose and fructose conversion into 5-hydroxymethylfurfural (5-HMF) is an essential step in biomass valorisation, offering a sustainable pathway to bio-based compounds. In this study, a single-phase and biphasic catalytic system was explored for processing diverse feedstock molecules to produce 5-HMF. Through extensive catalyst screening, it was determined that solid acid catalyst, MCM-41-type material like Al-MCM-41 (Si/Al = 100), exhibit the highest efficiency for this conversion. Optimized reaction conditions, including catalyst loading (20–30 wt% of the substrate), water-to-substrate ratio (25–30), and reaction parameters (160–170°C for 6–12 hours), resulted in crude 5-HMF yields of 40–50 mol%. After purification using $NaHCO_3$ to remove acids, the pure 5-HMF yield was 20–25 mol%. Despite these promising results, significant challenges remain, including the complex analysis and isolation processes and the inherent instability of 5-HMF, which leads to secondary by-products such as organic acids. These findings underscore the potential of MCM-41-based catalyst for effective 5-HMF production while highlighting the need for improved separation and stabilization strategies.

Introduction:
The use of renewable biomass as a feedstock for the synthesis of chemicals with added value has received a lot of attention lately because of environmental issues and the diminution of fossil fuels. The abundant components of biomass, glucose and fructose, offer attractive starting points for the synthesis of high-value compounds like 5-hydroxymethylfurfural (5-HMF), a flexible platform chemical with a wide range of industrial uses [1,2]. Acidic catalysts are usually used to catalyse the dehydration occurrences that turn glucose and fructose into 5-HMF. Zeolites are among these catalysts and have shown to be effective candidates for this transformation due to their well-defined porous structure and adjustable acidity [3,4]. Zeolite catalysts, particularly H-ZSM-5, provide special benefits for encouraging the specific dehydration of glucose and fructose into 5-HMF. The zeolite framework's acidic sites promote the dehydration reactions while reducing undesirable side reactions, improving 5-HMF yield and selectivity [5,6]. To enhance the efficiency of the conversion method, it is imperative to optimize the parameters of the reaction, such as temperature, pressure, catalyst loading, and solvent selection [7]. Furthermore, the catalytic activity and selectivity towards the synthesis of 5-HMF can be greatly influenced by the selection and modification of the zeolite catalyst [8,9]. 5-HMF is a significant chemical intermediate used in the synthesis of many different kinds of compounds, such as polymers, fine chemicals, and biofuels [10]. Its production from renewable biomass via zeolite catalysed conversion promotes the possibility of the development of more environmentally friendly and commercially successful chemical processes in addition to contributing to the sustainable use of resources [11]. Heterogeneous catalysts like, zeolites and MCM-41 type materials, plays a vital role in the effective synthesis of 5-hydroxymethylfurfural (5-HMF) from renewable biomass. Heterogeneous catalysts offer several advantages, including easy separation from the reaction mixture, reusability, low catalyst-product residue and the ability to control reaction selectivity and yield due to their well-defined structures and acidic sites [12-15]. Their usage in the dehydration of glucose and fructose to 5-HMF promotes higher

efficiency and selectivity while minimizing side reactions. The conversion of Glucose/Fructose into 5-HMF by using solid acid catalyst was done by several researchers [16,17]. Several types of catalyst, mechanism and reaction conditions have been studied by many researchers in an effort to enhance the yield and selectivity [18-20]. The main focus of this study is to optimize the catalytic conversion of glucose and fructose into 5-hydroxymethylfurfural (5-HMF) using solid acid MCM-41-based catalysts, aiming for high efficiency and yield. It also tries to find challenges in product stability, purification, and by-product formation for more sustainable biomass valorisation [21-23].

Materials and methods:

Techniques

"X-ray powder diffraction data was acknowledged on a Bruker AXS D8 Advance diffractometer using a graphite monochromator with Våntec-1 detector and Cu Kα radiation (at 40 kV and 30 mA) in Bragg-Brentano geometry". The textural characteristics of mesoporous Si-MCM-41 and Al-MCM-41 were characterized from nitrogen adsorption isotherm at -196°C through Micrometrics ASAP 2020. Shimadzu LC 2050 HPLC with C18 reverse phase column was used for the analysis of reaction products.

Synthesis of Si-MCM-41

Synthesis of Si-MCM-41 was done by hydrothermal method in alkaline medium using molar gel composition, 1 SiO2: 0.33 TMAOH: 0.55 CTMABr: 60 H2O as per published method [24]. Add 20.83 gm of Tetraethyl orthosilicate (TEOS) into aqueous solution containing 20.043 g of cetyltrimethylammonium bromide (CTMABr) and 12 g of 25 % tetramethylammonium hydroxide in water under continuous stirring. After five hours of constant stirring, the mixture was placed in a Teflon-lined autoclave and heated to 383 K under autogenic pressure for five days to ageing. After filtering and washing with distilled water, the product was allowed to air dry at room temperature. For eight hours, the as-synthesised material was calcined in air at 823 K in a furnace that gradually increased its temperature from room temperature at a rate of 1 K/minute. The yield was observed 5.85 g for Si-MCM-41, after the calcination.

Synthesis of Al-MCM-41

Al-MCM-41 sample was made with the molar gel composition 1 SiO2: 0.33 TMAOH: 0.55 CTMABr: 60 H2O: x Al2O3, where x ranges from 0.025 to 0.0005 moles. The catalyst Al-MCM-41 (100) was prepared using similar process as Si-MCM-41, with the exception that aluminium sulphate was added to the final gel and stirred for five hours. The gel was kept in autoclave at 383 K for 5 days for ageing. For eight hours, the as-synthesised sample was calcined in air at 823 K in a furnace that gradually increased its temperature from ambient at a rate of 1 K/minute [24]. The yield was observed 6 g for Al-MCM-41, after the calcination.

X-ray Diffraction pattern for Si-MCM-41:

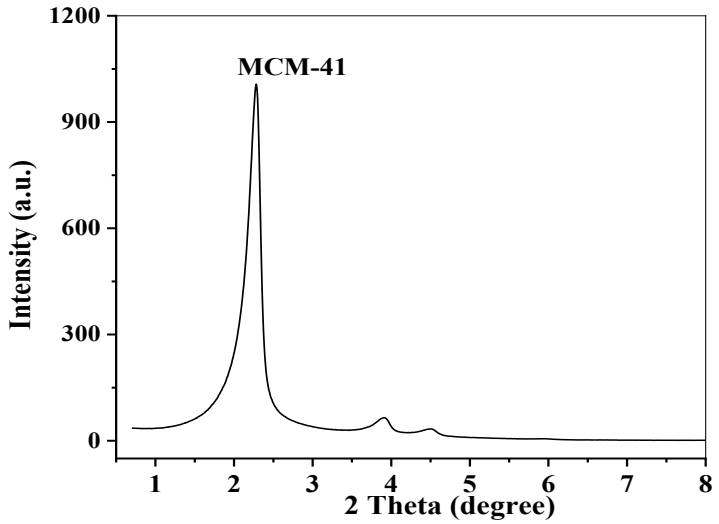

Figure 1: XRD of MCM-41.

It can be seen in Fig. 1 that MCM-41 exist in well-defined lattice. X-ray diffraction showed diffractogram with limited number of reflections which are situated at low angles. It was observed that three reflections were well resolved which corresponds to (100), (110), (200) reflections. The last reflection corresponding to (210) indicates diffraction peak with lower intensity. The size of hexagonal unit cell of mesoporous MCM-41 can be calculated from the reflection angles. Among all reflections, (100) is more intense and (210) is the least intense reflection. These reflections were indexed by Kresge et al. [25,26] for a hexagonal unit cell whose parameters were determined by applying the formula ao = d100/√3. Table 1 presents the result of XRD study for Si-MCM-41 and Al-MCM-41.

Table 1: XRD Analysis for Si-MCM-41 and Al-MCM-41.

Sample	d_{100} (Å)		Unit Cell Parameter` a_0 (Å)		Wall Thickness (Å)
	As synth.	Cal.	As synth.	Cal.	
Si-MCM-41	36.8	35	42.6	40.6	11.8
A-MCM-41 (110)	37.8	33	44	37	9.8

Calculated by the equation: a_0= 2d100/Ö3; b-Wall thickness = a_0 - Pore diameter

Nitrogen sorption:

The adsorption isotherm of Si-MCM-41 and Al-MCM-41 are typically type IV adsorption isotherm and hysteresis loops corresponding to mesoporous materials.

Table 2 shows surface area and pore diameters for Si-MCM-41 and Al-MCM-41 (100). It has been observed that, BET surface area for Si-MCM-41 and Al-MCM-41 (100) was 1096 and 1220 m^2/g respectively [27,28]. It was supposed that the BET equation would not be accurate to derive the surface area for mesoporous material with narrow pore diameters like MCM-41 because of possibility of limited adsorbate layers on the surface. N_2 adsorption and desorption isotherm revealed that, mesoporous materials possess uniform pores with narrow pore size distribution. However, the distribution becomes broader due to greater disorder arising from the introducing of Al atom inside the silica wall.

Table 2: Physicochemical properties of Si-MCM-41 and Al-MCM-41 (100).

Sample	S_{BET} (m^2/g)	Pore Diameter D_{BJH} (Å)	Pore Volume V_{BJH} (cc/g)
Si-MCM-41	1096	28.7	0.79
Al-MCM-41 (100)	1220	27.4	0.84

Result:

The synthesis of mesoporous materials has made new possibilities for preparing heterogeneous catalysts containing uniform pores with high surface area and high pore volume. The catalytic reactions were carried out in parr type closed autoclaves at autogenous pressure. The reactions were carried out using different catalysts and solvents. Initially toluene was used as a solvent particularly with zeolite catalysts, mainly to avoid secondary reaction, which lower the selectivity of primary product 5-HMF [29,30]. Reaction temperature was also varied. After preliminary testing, reaction temperature = 160°C, Reaction time = 1-4 h, Catalyst wt. = 0.5 wt. %, solvent = toluene (water to be tried next), nitrogen purge was chosen for further testing.

Two layers are formed when toluene was used as a solvent. The organic layer was analysed by U.V. detector and aq. layer were analysed by R.I. detector. The standardization and quantification of the HPLC analysis set up was also carried out for both the UV and RI detector systems. The results of preliminary catalysts screening are summarized below in Figure 2.

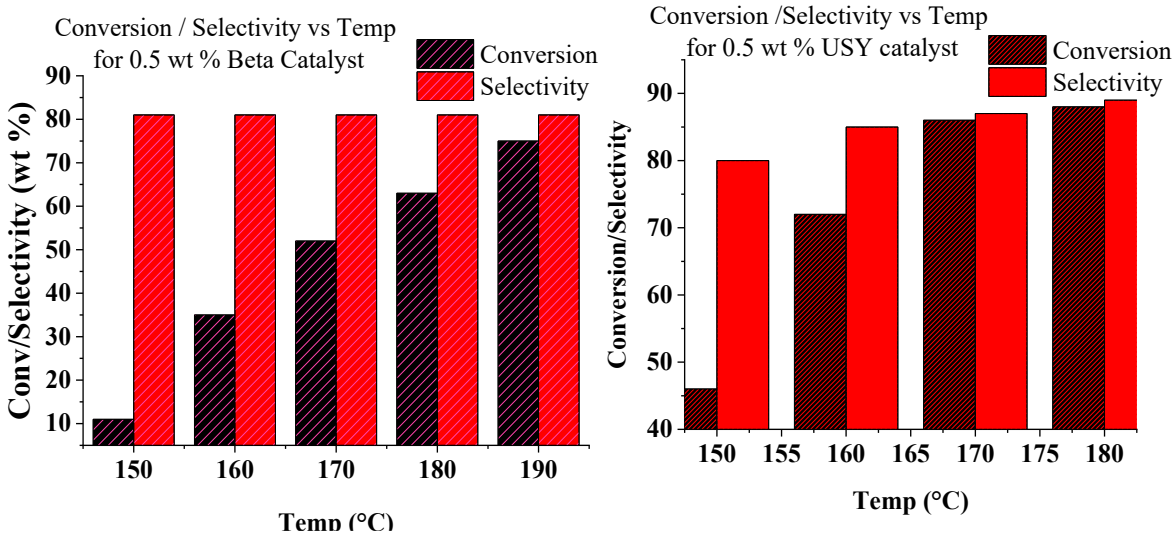

Figure 2: Effect of catalysts, catalyst amount and reaction temperature.

Reaction conditions: Glucose 3.75 g, water 50g, toluene 116.25 g, reaction time 2 h.

The HMF reactions were carried out at different temperatures ranges from 150°C to 190°C by taking different catalyst wt. % ratios. However, the maximum glucose conversion was obtained at 190°C with 81 % HMF selectivity and glucose conversion was 75 wt. % using Beta (Si/Al = 25) catalyst. When USY catalyst was used, the maximum conversion was obtained at 180°C with 81% HMF selectivity and glucose conversion wt. % with 88 %. The reaction product was analysed by HPLC with mobile phase; methanol:water = 70:30. At 190°C there are no conversion and selectivity for USY catalyst. The HPLC analysis was carried out at 50:50 (wt. %) (instead of 70:30 wt. %) methanol:water mixture as mobile phase. The low selectivity for 5-HMF using 50:50 (wt. %) methanol:water as mobile phase was due to proper separation of 5-HMF and furfural.

Identification and quantification of products using standard mixtures:

Four standard samples containing different amounts of toluene and 5-HMF were prepared and analysed for quantification. Similarly, four standard samples containing different amounts of 5-HMF and water were prepared and analysed by HPLC (UV and RI) detectors for quantification. Aqueous and organic layer were analysed by following reaction conditions. Aqueous Layer: R.I. detector: (waters RI2410), Column: sugar Pak-I, Mobile Phase: Ca-EDTA, 0.005%), Flow = 0.4 ml/min. Organic Layer: UV-detector (Shimadzu LC 10A), Column: C-18 reverse phase.

During HPLC analysis, it was found that the separation between 5-HMF and furfural (by product) is not satisfactory and hence the mobile phase (methanol:water) composition was varied and the standard sample was analysed. The results are given below in Table 3. The best separation was obtained when methanol:water ratio was 50:50 (wt. %).

Table-3: Screening of Mobile phase on the separation of 5- HMF and furfural using UV-detector (Shimadzu LC-10A), Column = C-18 reverse phase, Mobile phase = x methanol: y water (flow rate: 1 ml/min).

Mobile phase (wt.%)		Product separation of 5-HMF and furfural
X Methanol	Y Water	
70	30	No separation
60	40	Broad Overlapping Peaks
50	50	Separation was fairly okay
40	60	Broad overlapping peaks

Hence in all subsequent analyses, 50:50 methanol:water mixture (wt. %) was taken as mobile phase for HPLC analysis using UV detector. Acetonitrile and water (70:30 wt. %) were also tried and it was found to be not suitable.

There are certain advantages when the reaction is carried out in single liquid phase, particularly when the reaction can be carried out in water as reaction medium. It is clear from above table that, both glucose conversion and the 5-HMF selectivity were higher in aqueous medium compared to toluene-water biphasic liquid system. Hence in all subsequent experiments, water is used as solvent. The results are summarized in Table 4 and it was observed that Al-MCM-41 (100) shows higher selectivity and isolated yield for glucose substrate as comparatively other catalysts. The crude isolated product was ca. 95% pure (remaining is mainly furfural).

Table 4: Water as solvent for the catalytic reactions. Reaction conditions: Glucose = 8.5g, water = 290g, catalyst = 1.5 g, Temp = 160°C, time 6 h, N2 = pressure (100 psi), rpm = 300 (Mass Balance = 95 %).

Catalyst	Substrate	5-HMF Selectivity, wt.%	Isolated Yield (mole % of glucose
USY	Glucose	60	28
Ti-MCM-41 (40)	Glucose	85	34
Ce-MCM-41 (40)	Glucose	80	30
Al-MCM-41 (100)	Glucose	95	60
Al-MCM-41 (100)	Fructose	95	80
Al-MCM-41 (100)	Glucose (Reflux)	0	0
Al-MCM-41 (100)	Fructose (Reflux)	0	0

Studies on the extraction of 5-HMF from reaction mixture:

Different solvent systems were tried for developing a most suitable solvent system for extracting the product 5-HMF from the aqueous reaction mixture. The results are summarized below in Table 5.

Table 5: Extraction of 5-HMF from reaction mixture.

Sr. No.	Solvent system used	Extraction result
1	Toluene	Moderate
2	Benzene	Moderate
3	Diethyl ether	Poor
4	DCM	Poor
5	Chloroform	Poor
6	DCM: Methanol (10%, 20%, 30%)	Poor
7	CHCl3 / MeOH (10%, 20%, 30%)	Good, with 30% CHCl3/MeOH
8	CHCl3 / IPA (10%, 20%, 30%)	Poor
9	CHCl3 / Ethyl Acetate (10%, 20%, 30%)	Poor
10	Ethyl acetate	Best or better than all tested solvent system

Since, ethyl acetate was found to be a quite suitable solvent, the extraction of the product was henceforth carried out using ethyl acetate as solvent. The isolated yields were obtained by evaporating the solvent using rotavapor.

Studies at different reaction temperature:

An isolated yield was investigated by using Al- MCM-41 (Si/Al=100) at different reaction temperatures. It was clearly seen that, Al-MCM-41 (100) shows better yield at 170°C as compared to at 140, 150, 160 and 180°C. The isolated yield at 160°C and 180°C shows slightly lower (42%) compared to 170°C temperature, which shows 45% of isolated yield.

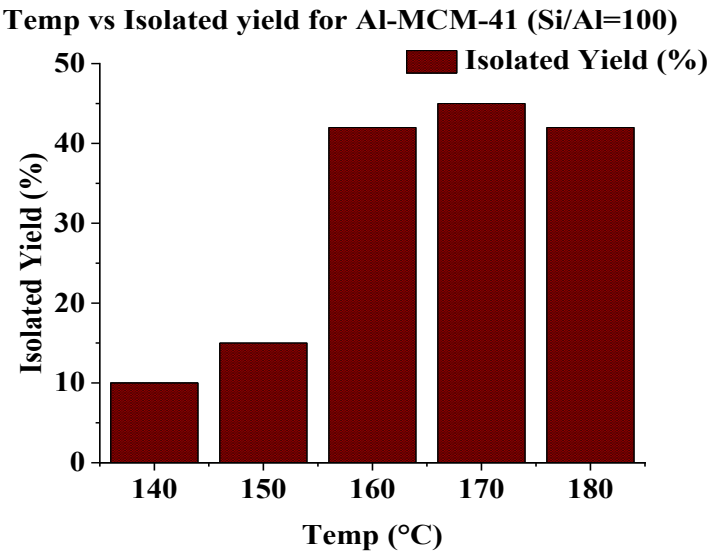

Figure 3: Effect of reaction temperature using Al-MCM-41 (Si/Al=100).

Effect of reaction time:

Time dependent study on Al-MCM-41 (100) was carried out at 170°C to find out the optimum time for obtaining maximum yield of 5-HMF can be summarized in following Table 6.

Table 6: Effect of reaction time for Al-MCM-41 (100).

Catalyst	Temp, °C	Time, h	Isolated Yield, %
Al-MCM-41 (Si/Al = 100)	170	3	30
Al-MCM-41 (Si/Al = 100)	170	6	45
Al-MCM-41 (Si/Al = 100)	170	9	47
Al-MCM-41 (Si/Al = 100)	170	12	50

As shown in Table 6, it is clearly indicating that as the time increases, the yield is also increases and at certain level yield will be constant. If reaction is proceeded further then there are some chances to get decomposition of the product.

Studies on the optimization of extraction of 5-HMF:

To optimize the extraction with solvent (ethyl acetate) with high extracting efficiency, various experiments were done. It was found that repeated extraction with smaller aliquots of ethyl acetate is more efficient. The isolated yields were obtained by evaporating the solvent using rotavapor, dried under vacuum. It is clear that the catalyst should possess very mild acid sides in order to achieve moderate to good isolated yields of 5-HMF.

Effect of catalyst with reusability of aqueous layer:

The catalytic activity of Al-MCM-41 (Si/Al = 100) clearly indicate that Al-MCM-41 (100) catalyst produce comparable moderate to high isolated yield of 5-HMF.

Table 7: Reusability of Al-MCM-41 (Si/Al=100), Temp = 170°C, Time = 12 h, 4.5 g glucose, catalyst = 0.9g (20 wt. % of glucose), 144.6 g water (total reactants = 150g).

Catalyst	5-HMF, isolated yield, mole %			
	First Cycle	Second Cycle	Third Cycle	Total
Al-MCM-41 (Si/Al=100)	48	15	5	68

Extracted aqueous layer was diluted to 150 ml (along with catalyst amount) and further reacted under same reaction conditions. The reusability of Al-MCM-41 (Si/Al=100) was carried out in glucose/fructose conversion into 5-HMF. Extracted aqueous layer was diluted to 150 ml (along with catalyst amount) and further reacted

under same reaction conditions. The catalyst was used three times. As shown in Table 7, it is clearly indicating that Al-MCM-41 (100) shows good yield. After first cycle HMF isolated yield was up to 48% where 15% after the second cycle. The total yield was observed 68% after the third cycle. However, there are some advantages of Al-MCM-41 type materials with good reproducibility.

For the conversion of glucose to HMF, Al-MCM-41 (Si/Al=100) is beneficial because it provides a well-balanced combination of Lewis and Bronsted acid sites within ordered mesoporous molecular structure. This permits for the efficient isomerization of glucose to fructose (a Lewis acid site) and triple dehydration to HMF (a Bronsted acid site) within the catalyst, ensuing in high HMF yields with good selectivity. Moreover, the large surface area and pore size of MCM-41 help to improve catalytic activity by facilitating diffusion of reactants and products easily.

Conclusion:

This study demonstrated that both single-phase and biphasic catalytic systems are effective for the conversion of glucose and fructose into 5-HMF by using solid acid catalysts with mild acidity. Al-MCM-41 (Si/Al = 100) has demonstrated superior catalytic performance under optimized reaction conditions (160-170°C, 6-12 hours), attaining crude 5-HMF yields of up to 50 mol% and purified yields of 20-25 mol% with $NaHCO_3$ washing. Despite of these advancements, challenges persist in product separation, characterization, and stability, as 5-HMF readily undergoes side reactions leading to undesired acidic by-products. Overcoming these limitations is crucial for enhancing process viability and scalability in sustainable biomass valorisation.

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Declaration of completing interest:

The author declares that there are no conflicts of interest regarding the publication of this paper.

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Authors Contributions :

Tushar Shinde : All the experimental work, scientific investigations, writing of the manuscript along with writing review and editing of the manuscript.

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