

Efficient Conversion of Carbohydrates to 5-Hydroxymethylfurfural over Mesoporous Zeolites

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Abstract

The conversion of carbohydrates to 5-hydroxymethylfurfural (5-HMF) in a biphasic system have been studied by using various H-form zeolite catalysts. The biphasic reactor system consists of aqueous phase and organic phase (1:2 w/w). The aqueous phase which contains of feed stock, catalyst, sodium chloride (NaCl), Deionized water (dH2O) and an organic phase which contains the methyl-isobutyl-ketone (MIBK). The effects of different factors, such as the type of catalysts, reaction temperature and reaction time, on the yields of 5-HMF have been studied systematically in the biphasic system. The catalysts have been characterized by various analytical techniques (XRD, FETEM, N₂-Sorption, Py-FTIR, and NH₃-TPD) to study on crystal structure, morphology, acid properties, and texture, respectively. Among the catalysts tested, H-Beta showed the highest 5-HMF yield of 94% with a fructose conversion of 98%. The highest selectivities to 5-HMF obtained with the glucose (74%) and cellulose (41%) substrates are, respectively, at 180°C. The H-Beta showed excellent stability without any deactivation even after 5 cycles have been reused.

Keywords: Carbohydrates, 5-Hydroxymethylfurfural, Biphasic system, Zeolites

INTRODUCTION

The research on biomass conversion to value-added chemicals is gaining significant attention in recent years. The second generation (lignocellulosic) biomass such as agricultural and forest residues, contains cellulose, hemicellulose, and lignin as major building blocks.[1] The 5-hydroxymethylfurfural (5-HMF) is an important platform chemical that can be derived from biomass, particularly from cellulose which is a polymer of glucose.[2] The 5-HMF has numerous applications in polymers, solvent industries, and biofuels.[3]

5-HMF could be produced from fructose, an isomer of glucose, with high yields.[3a] However, it is costlier and less abundant. Therefore, the direct conversion of glucose and cellulose to 5 HMF has been explored. However, this process requires the presence of both Brønsted and Lewis acid sites. However, some researchers reported a mechanism which suggests the direct conversion of glucose to 5-HMF without the formation of fructose, which indicates that only Brønsted acid sites are sufficient for the reaction.[4]

In the early years, homogeneous catalysts have been explored for direct conversion of glucose and cellulose to 5-HMF. Mineral acids such as H₂SO₄ and HCl are tested for this reaction, but obtained low yields (13% with H₂SO₄[5] and 10% with HCl[6]). Metal chlorides such as CrCl₃ alone also resulted in low yields (≈10%).[7] Higher yields are reported when CrCl₃ is used in combination with ionic liquids (IL) or mineral acids (>70% with IL[8] and 59% with HCl[9]). The major issues in using the above mentioned recycle. In contrast, solid acid catalysts have numerous advantages over homogeneous catalysts in terms of product separation, catalyst-life, -recovery, and -recycle.[1a, 3b, 10]

Zeolites have also been studied for this reaction.[3b] Hu et al.[11] studied various zeolites with IL ([BMIM]Cl) as a solvent, and reported 50% yield of 5-HMF from glucose over Beta zeolite. Otomo et al.[12] tested the Beta zeolites calcined at different temperatures for glucose dehydration. The authors claimed that the high calcination temperatures (750°C) resulted in higher yields of 5-HMF (55%) due to the generation of Lewis acid sites. Most of the studies on zeolites as well as other solid acid catalysts involve the use of either dimethyl sulfoxide (DMSO) or IL as solvents.[3b, 13] However, these high boiling solvents require high energy for the product (5-HMF) separation from them.

In the present study, zeolite catalysts i.e., H-Beta, H-MOR, H-Y, and H-ZSM5 have been tested for the conversion of carbohydrates (fructose, glucose, and cellulose) to 5-HMF in a biphasic system containing eco-friendly solvents (water as reaction phase and Methyl isobutyl ketone (MIBK) as extraction phase). The effect of reaction conditions such as reaction time, temperature, and the substrate on conversion and yield is studied. Further, the stability (recyclability) of the best catalyst is investigated in this work.

I. MATERIALS AND EXPERIMENTAL SECTION Reagents and chemicals

All the zeolite catalysts, i.e., H-Beta (SiO₂/Al₂O₃ mole ratio 360:1), H-Y (80:1), NH₃-ZSM5 (80:1), and NH₃-MOR (20:1) were obtained from Alfa Aesar, the USA. The NH₃ forms of ZSM5 and MOR were converted to H-form by calcining at 400°C for 2 h. Cellulose, fructose (99.5%), glucose (99.5%), and acetic acid (98%) were supplied by Hi-media, India. Formic acid (98%) was supplied by Loba Chemie, India. 5-HMF (98%) was supplied by SRL, India. Silicone oil, levulinic acid (97%), H₂SO₄ (99%), NaCl (99%), 1,4-dioxane (99.5%), and methyl isobutyl ketone (99%) were procured from Merck, India. All the chemicals were used as supplied without further purification. Deionized water (dH₂O) is obtained from the Millipore water purification unit (Model: Elix-3 Milli-Q, Make: Millipore, France).

Catalyst characterizations

X-ray diffraction(XRD) patterns of zeolites were recorded using X-ray diffractometer (Model: D8 Advance, Make: Bruker, Germany) at a Cu-K α radiation of 1.5406 Å in a 2 θ range of 5-50° with 0.05° step size and scan speed 1 s⁻¹. Surface morphology of catalyst particles was obtained using FETEM instrument (Model: JEM-2100F, Make: JEOL, Japan). A small

amount of catalyst was dispersed in 5 mL acetone and placed in an ultrasonic bath for about 30 min to segregate individual particles. After sonication, one drop of suspension was deposited onto a carbon-coated copper grid, and the film on TEM grid was left for 2 min. The grid was then allowed to dry in a vacuum desiccator for overnight at room temperature.

The textural properties were studied by the N₂-sorption experiments at -196°C (77K), using a Gas adsorption analyzer (Model: Autosorb-IQ MP, Make: Quanta chrome, USA). Prior to N₂ sorption experiments, the samples were degassed at 200°C for 4 h. The surface areas of catalysts were calculated by using the Brunauer-Emmet-Teller (BET) equation. Mesopore volume and size distribution were calculated with Barrett-Joyner-Halenda (BJH) method. Micropore volume and surface area were determined by the t-plot method. The concentration of Brønsted (CBAS) and Lewis acid (CLAS) sites was measured by Fourier transformed infra-red spectrometer (Model: IR Affinity 1, Make: Shimadzu, Japan) in a wavelength range of 1400 – 1600 cm⁻¹ with 30 scans and a resolution of 4 cm⁻¹, using pyridine as a probe molecule. The samples were first heated to 400°C for 1 h, cooled to ambient temperature under a vacuum and then purged with N₂. The pyridine was injected under the N₂ atmosphere at room temperature. After soaking the sample in pyridine for about 30 min, the excess pyridine was removed by evacuation at 100°C for 2 h. The CLAS and CBAS were calculated using the extinction coefficients reported by Emeis.[23] The total acidity of the samples was also determined using ammonia temperature programmed desorption (NH₃-TPD, Model: BELCAT-II, Make: MicrotracBEL, Japan) equipped with a thermal conductivity detector (TCD). In a typical analysis, the sample was pretreated at 400°C for 1 h under helium (He) gas flow (50 mL.min⁻¹) and then cooled to 50°C. The sample was saturated with 10% of NH₃/He mixture for 60 min at 50°C. The physisorbed NH₃ was removed under helium flow at 100°C for 10 min. Finally, desorption of ammonia was carried out in the temperature range from 100 to 800°C with a heating rate of 10°C.min⁻¹ under helium flow

Catalyst Activity Tests

The detailed catalyst testing procedure is presented in our previous work.[24] In a typical experiment, a reaction phase, containing required amounts of carbohydrate (cellulose, glucose or fructose), NaCl, dH₂O, and zeolite, was introduced into a Teflon lined stainless steel autoclave reactor. A required amount of immiscible extracting solvent (MIBK, extraction phase) was added to the reaction phase. The reactions were performed in a temperature range of 160 – 180°C under stirring (600 rpm) for 1-4 h.

After the experiment, the reaction was quenched by immersing the autoclave in an ice bath. The solid catalyst, the insoluble solid products (such as humins) and the unreacted cellulose (when cellulose is used as a reactant) were separated by filtration followed by separation of reaction and extraction phases. A portion of the reaction phase was pipetted out and diluted (1:5 w/w) with dH₂O. Similarly, a portion of the extraction phase is pipetted out and diluted (1:0.5 w/w) with MIBK. The samples were analyzed by using a High-performance liquid chromatography (HPLC, Model: series 200, Make: Perkin Elmer, Switzerland), equipped with a quaternary pump, a refractive index (RI) detector, and a Hi-Plex H column (300 mm × 7.7 mm). The column temperature was set at 60°C. The mobile phase (0.01M aq. H₂SO₄) was pumped at a flow rate of 0.6 mL min⁻¹. Glucose, fructose, 5-HMF, lactic acid, formic acid (FA), and levulinic acid (LA) were quantified using 1,4-dioxane as an external calibration standard. The conversion of carbohydrate and yields of products were calculated using the following equations.

Carbohydrate conversion (%) = (Mass of carbohydrate reacted)/(Initial mass of carbohydrate) × 100

Yield (%) = (Moles of product formed)/(Initial moles of carbohydrate) × 100

Selectivity (%) = (Moles of product formed)/(Moles of carbohydrate reacted) × 100

In the case of cellulose, the yield is calculated based on the equivalent glucose units (molecular weight 162.14 g/mol)^[25] and the mass of carbohydrate (cellulose) reacted is calculated by subtracting catalyst mass from the dry solid filter-cake mass obtained after the experiment. All the experiments are repeated at least two times and average values are reported. The details of experimental conditions used in this study are summarized in Table S1. The carbon balance is always above 90 ± 5%, in the glucose and fructose experiments and is lower in the cellulose experiments (above 70%). The mass of carbon lost to coke or humins is less than 10%. In the case of cellulose, the remaining mass may be in the form of oligomers, which are not quantified in this study.

Catalyst stability test

The reusability of H-Beta catalyst was investigated at the optimal conditions (0.2 g cellulose, 2 g dH₂O, 4 g MIBK, 0.6 g NaCl, 0.067 g catalyst, 180°C temperature, and 3 h reaction time). The catalyst sample obtained after each reaction was washed two times with dH₂O (5 mL) and used in the next experiment without any further treatment.

RESULTS AND DISCUSSION Catalyst Characterization

The XRD patterns of H-Beta, H-MOR, H-ZSM5, and HY (Figure 1) are matched with the patterns typically found for these catalysts.[14] N₂ sorption isotherms of all the zeolites are shown in Figure S1 of the Supporting Information (SI). As expected, all the zeolites are exhibited type IV isotherms, and both micropore and mesopore textures. This is in accordance with the literature.[14a] The ratio of mesopore to micropore surface area varied significantly among the catalysts (Table 1). For example, for H-MOR, the ratio of micropore to mesopore area is 14.5, whereas that for H-Beta is 1.49. The BET surface area of H-MOR is nearly equal to that of H-ZSM5. However, the micropore area and micro to mesopore volume ratio of H-MOR are higher than those of H-ZSM5. The average pore size of all the zeolite catalysts is in the similar range of 2.8–3.2 nm. Eventhough H-ZSM5 has 10-membered ring structure, the average pore size is similar to that of other 12-membered ring zeolites. The NH₃-TPD patterns are shown in Figure S2a. All the zeolites except H-MOR exhibit three distinct peaks corresponding to ammonia desorbed from weak, moderate and strong acid sites of the zeolites. Based on the peak temperatures and the corresponding quantity of ammonia desorbed, the acid strength is found to be in the following order: H-MOR > H-Beta > H-Y > H-ZSM5. The NH₃-TPD patterns of the zeolites and their acid strengths are similar to those reported in the literature.[15] The total acidity from NH₃-TPD varied as follows: H-MOR > H-BETA ≈ H-ZSM5 > H-Y (Table 2). From Py-FTIR spectra, it can be observed that the C_{LAS} is increased and C_{BAS} is decreased with the SiO₂/Al₂O₃ ratio (SAR) (Table 2 and

Figure S2b). The highest C_{BAS} observed with H-MOR zeolite may be due to the higher Al concentration (lower SAR). The higher Al concentration accommodates more protons, which in-turn results in higher Brønsted acidity.^[16]

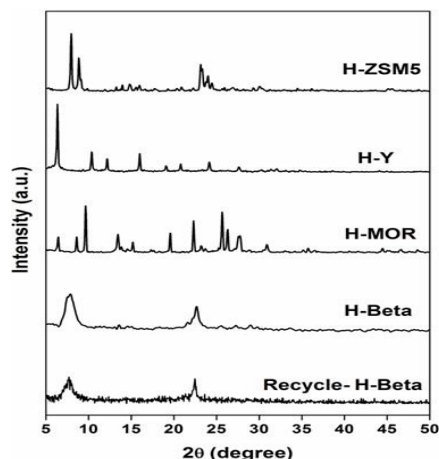


Figure 1: The powder XRD patterns of various zeolite catalysts used in this study

Performance of Various Zeolite in Glucose to 5-HMF Conversion

The effect of reaction temperature (in the range of 160 – 180°C) and reaction time (1.5 – 3 h) on glucose conversion and product yields over H-ZSM5 is shown in Figure 2. The reaction temperature has a significant influence on glucose conversion as well as on the yield of 5-HMF. The glucose conversion and 5-HMF yield are increased from 16% to 71% and from 12 to 46%, respectively, with the temperature. The yields of other reaction products such as LA and FA are increased and that of AA is nearly constant ($\approx 3\%$) with the temperature. The selectivity to 5-HMF is first increased and then decreased, and selectivities to LA and FA are increased, with the temperature. This implies that H-ZSM5 favours the rehydration of 5-HMF to LA and FA at high temperatures.

With the reaction time, the glucose conversion is increased from 64% to 96% and the yield of 5-HMF is exhibited a maximum of 46% at 2 h (Figure 2b). The yields of LA and FA are increased with the prolonged reaction time, indicating that the higher residence time is not favourable for the selective conversion of glucose to 5-HMF.^[17] Therefore, a reaction temperature of 180°C and a reaction time of 2 h are found to be the optimum.

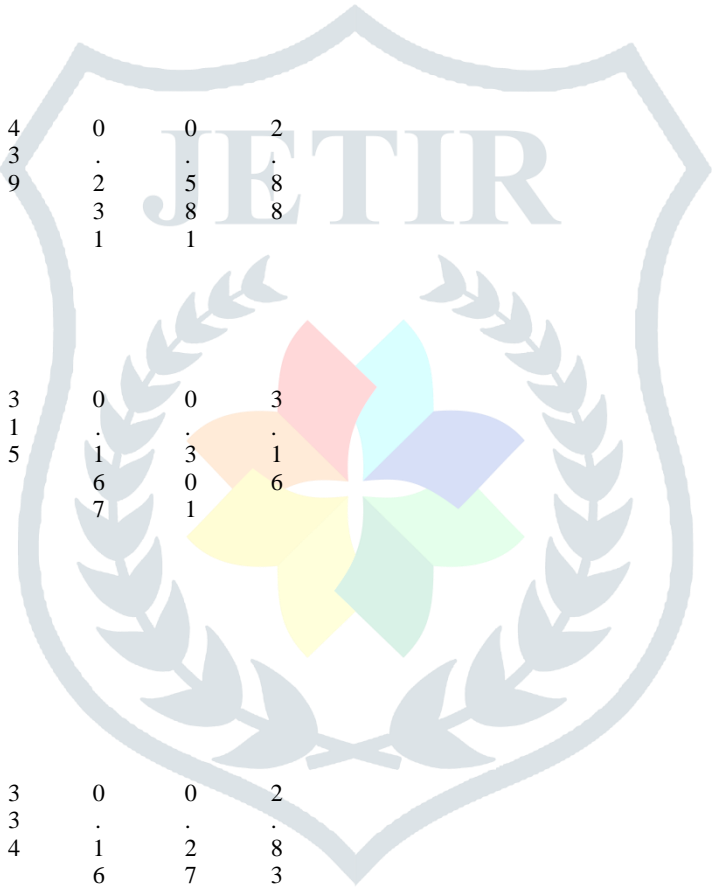
The glucose conversion and yields of different products over H-Beta, H-MOR, H-Y, and H-ZSM5 at identical reaction conditions (Table S1, Exp. nos: 2, 7 – 9) are shown in Figure

3. No traces of fructose (not shown in the figure) are found in the reaction products. This indicates that the fructose is converted to 5-HMF soon after its formation and/or the reaction proceeds through either open-chain or cyclic mechanism where no formation of fructose could be observed. Among the zeolites tested, H-MOR and H-Beta are exhibited the highest and the lowest conversion, respectively. The yield of 5-HMF followed an opposite trend and is the lowest over H-MOR and the highest over H-Beta. The higher mesoporosity (as evidenced from the N_2 -sorption data, Table

1) may be a reason for the higher yield of 5-HMF with H Beta zeolite which is having high SAR and low C_{BAS} . The micropore surface area may not be accessible to the reaction due to the larger molecular sizes of reactant and products of the present study. Even if it accessible by the acyclic hexose molecule, the 5-HMF formed may rearrange to higher molecular weight compounds or to will rehydrate to form LA and FA.^[10] The catalyst having higher mesoporosity is expected to show a higher yield of 5-HMF^[18] and that is what we observed in this study. For example, the H-Beta ($S_{BJH} = 223 \text{ m}^2/\text{g}$) shows a higher yield of 5-HMF (46%) as compared to that (36%) over H-MOR ($S_{BJH} = 23 \text{ m}^2/\text{g}$). However, the mesoporosity is not playing any role in enhancing the glucose conversion. The lower conversion over H-Beta could be attributed to the lower C_{BAS} , as evident from the Py-FTIR. The yields of LA and FA are significantly higher with H-MOR as compared to that on other zeolites. The higher C_{BAS} of H-MOR may be responsible for the side products formation by rehydration of 5-HMF.^[18b] Though the yields of 5-HMF are similar over the zeolites H-Beta (45.9%) and H-ZSM5 (45.6%), the selectivity is significantly higher with the H Beta (73.6% vs. 63.8%). Therefore, the H-Beta is used in further study.

Table 1: Textural properties of the catalysts used in this study

Zeo- lite (SAR ^a)	S _{BET} ^b	S _{BJH} ^c	V _{BJH} ^d	S _{t-plot} ^e	V _{t-plot} ^f	V _{TP} ^g	P _{hD} ^h
H-beta (360:1)	563	223	0.206	333	0.179	0.388	2.82
H-Y (80:1)	773	113	0.229	439	0.231	0.588	2.88
H-ZSM-5 (80:1)	381	70	0.133	315	0.167	0.316	3.16
H-MOR (20:1)	386	23	0.093	334	0.164	0.273	2.83



^aSAR - SiO₂/AlO₃ ratio

^bS_{BET} - BET surface area

^cS_{BJH} - BJH mesopore surface area from desorption

^dV_{BJH} - BJH mesopore volume from desorption

^eS_{t-plot} - t-plot micropore surface area

^fV_{t-plot} - t-plot micropore volume

^gV_{TP} - total pore volume calculated at P/P₀ = 0.99

^hP_D - Average pore diameter**Table 2:** Acid site concentration from Py-FTIR and NH₃-TPD analysis

S · N o ·	C a t a l y s t (S A R ^a)	C B A S (μ m o l .g ⁻¹) ^b	C _L A S (μ m o l .g ⁻¹) ^b	B / L r a t i o b	Total acid site concentrati on ^c (μmol NH ₃).g ⁻¹
1	H - B e t a (3 6 0)	1 1 9 · 2	4 8 4. 8	0 · 2 3	47
2	H - Y (8 0)	1 2 6 · 5	3 3 1. 4	0 · 3 9	36
3	H- Z S M 5 (8 0)	1 7 9 · 0	1 7 3. 1	1 · 0 3	44
4	H- M O R (2 0)	9 2 6 · 0	8 9 · 2	1 0 · 3 8	143

^aSAR - SiO₂/AlO₃ ratio

^bC_{BAS} (concentration of Brønsted acid sites), C_{LAS} (concentration of Lewis acid sites) and B/L (Brønsted acid sites/Lewis acid sites) ratio are measured using FTIR with pyridine as a probe molecule

^cTotal acid site concentration measured from the NH₃-TPD analysis

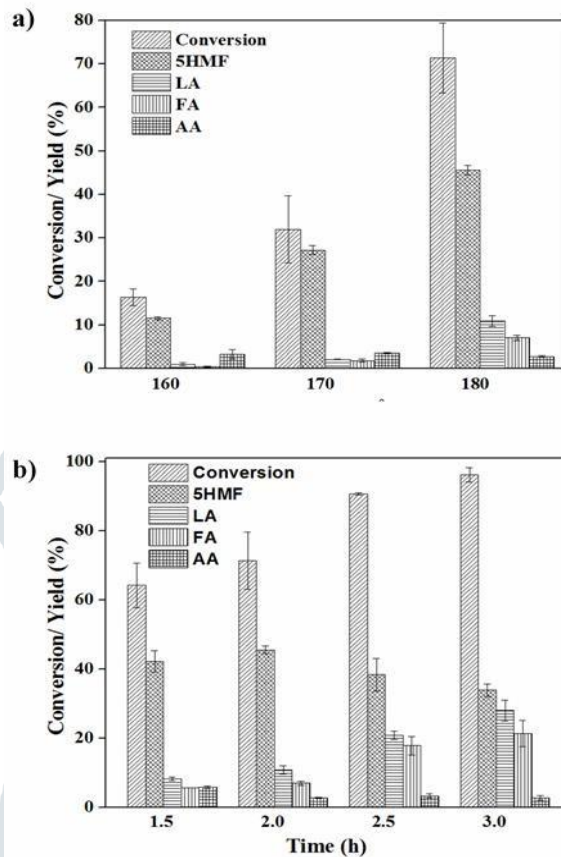


Figure 2: Variation of conversion of glucose and yield of reaction products (5-HMF, LA, FA, and fructose) as a function of (a) reaction temperature and (b) reaction time using H-ZSM5 catalyst

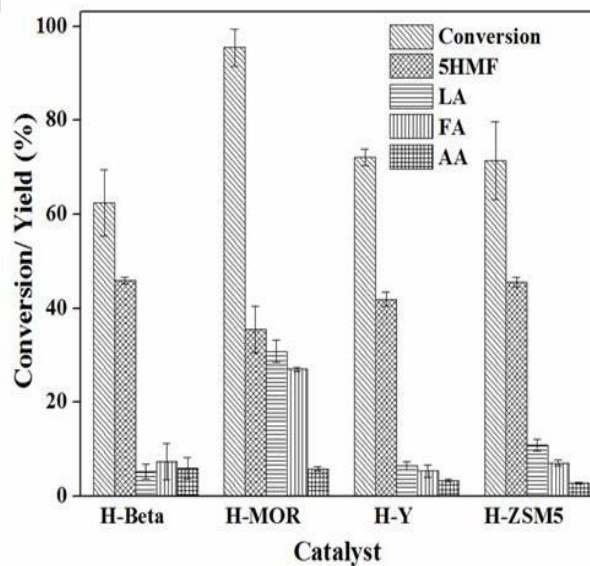


Figure 3: Conversion of glucose and yield of reaction products (5-HMF, LA, FA, and AA). (Reaction conditions: 2 g of DI water, 0.2 g of substrate, glucose:catalyst = 3:1 w/w, 4 g of MIBK, 0.6 g of NaCl, 2 h of reaction time, and 180°C of reaction temperature)

The effects of NaCl and presence of extraction phase on the conversion and yields are also studied over H-Beta (Table S1, Exp. nos: 10 – 13, Figure S3). The conversions of glucose (the yield of 5-HMF) without NaCl and in the presence and absence of extraction phase (MIBK) are 24% (16%) and 7% (5%), respectively. Whereas, the conversions of glucose (yields of 5 HMF) with NaCl and in the presence and absence of extraction phase (MIBK) are 62% (46%) and 63% (28%), respectively. Both extraction phase as well as NaCl have a significant synergistic effect on the conversion of glucose and yield of 5-HMF. The synergy can be attributed to two primary

reasons: (i) salting-out effect, which means upon the addition of NaCl to the biphasic system, the partition coefficient increases [17, 19] and (ii) reaction mechanism itself may change in the presence of NaCl.[20]

Mamo et al.[14b] compared glucose dehydration with differently modified mordenite zeolites in IL at 100°C for 6 h and reported a 5-HMF yield of 25% with similar pretreatment conditions of the catalyst used in this study. Otomo et al.[12] reported 5-HMF yield of 9.4% with water as a solvent and of 32% with DMSO, at 180°C and 3 h reaction time. Hu et al.[11] used H-MOR for glucose dehydration in the presence of IL at 140°C for 30 min and reported a very low 5-HMF yield of 13.1%. Therefore, based on the above comparison of previous studies with the present one, the toxic and uneconomical solvents (such as ILs and DMSO) can be avoided and still obtain better yields by using the mesoporous zeolite.

Performance of H-Beta with Different Substrates (Fructose, Glucose, and Cellulose)

The conversion of carbohydrate and yields of various products with the substrates (fructose, glucose, and cellulose) over H-Beta are shown in Figure 4. With fructose the reaction time used is 1 h and the other reaction conditions are identical (2 g DI water, 0.2 g substrate, substrate: catalyst = 3:1 w/w, 4 g MIBK, 0.6 g NaCl, and 180°C reaction temperature). With fructose as a substrate, the conversion is 100% and the yield of 5-HMF is 92%. The cellulose conversion is 99% and yields of glucose and 5-HMF are 38% and 35%, respectively. With glucose as substrate, the conversion is lower (62%) but the yield of 5-HMF is higher (45%) than that with the cellulose. The comparison of data from all the three substrates indicates that either the conversion of glucose to fructose or the direct conversion of glucose to 5-HMF is a rate-limiting step in the direct conversion of cellulose (or glucose) to 5-HMF. This hypothesis is also supported by the fact that in all the experiments (with glucose or cellulose as substrate) the fructose yield is zero. The yields of LA and FA are < 10% in the case of fructose and < 3% in the case of cellulose. The lower Brønsted acidity and the higher mesoporosity of H-Beta are favouring maintain lower yields of LA and FA by suppressing 5-HMF rehydration. The suppression of 5-HMF rehydration could, in-turn, be attributed to the good mass transport of the 5-HMF from the mesopores

The conversion of cellulose is nearly constant with reaction time (Figure 5). The yield of glucose is decreased with the reaction time and became negligible at 4 h. The yield of 5-HMF passed through a maximum at 3 h reaction time with a maximum yield of 40%. Therefore, the optimum reaction time for the cellulose to 5-HMF conversion is found to be 3 h at 180°C. Otomo et al.[21] reported a 5-HMF yield of 42% with H-Beta zeolite as a catalyst and in a solvent mixture of water, DMSO and tetrahydrofuran (THF) at 200°C for 5 h. Similar yield (46%) of 5-HMF from cellulose have been reported by Nandiwale et al.[18b] with a bimodal Micro/Mesoporous H-ZSM5 zeolite at 190°C for 4 h. Lanzafame et al.[22] reported a very low selectivity to 5-HMF from the cellulose of 10% at 190°C for 5 h. The conversion of the substrate and yield of 5-HMF are better or similar to those reported in the literature with similar catalysts. The better activity obtained in this study could be attributed to the mesoporosity or the framework topology of the H-Beta.

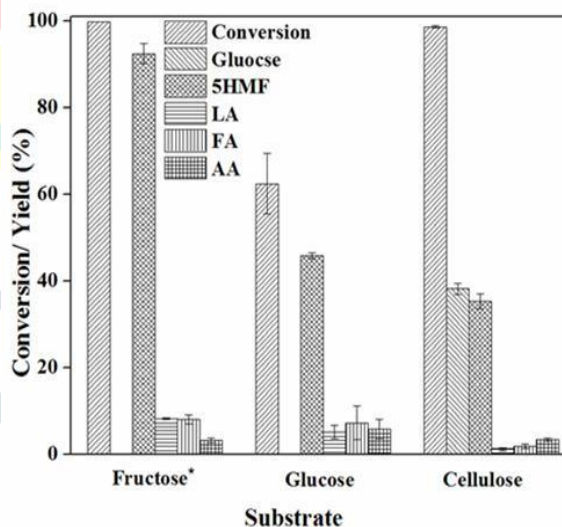


Figure 4: Conversion and yield of reaction products with various substrates (Fructose, Glucose and cellulose) over H-Beta zeolite catalyst (Reaction conditions: 2 g DI water, 0.2 g substrate, substrate:catalyst = 3:1 w/w, 4 g MIBK, 0.6 g NaCl, 2 h reaction time, and 180°C reaction temperature).

*With Fructose the reaction time is 1 h and other conditions are same as above. *Note: The yield of glucose from cellulose*

is also included.

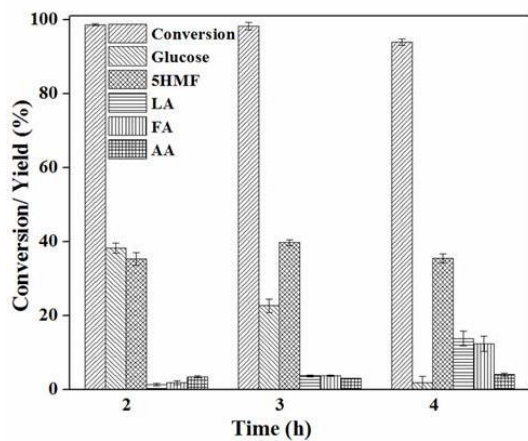


Figure 5: Conversion of cellulose and yields of reaction products as a function of reaction time over H-Beta

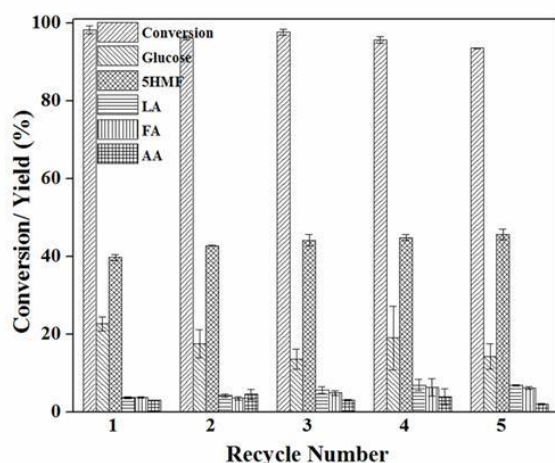


Figure 6: Conversion of cellulose and yields of reaction products as a function of catalyst recycle number over H-Beta

Recycle of Catalyst

The conversion of cellulose, as well as the yield of 5-HMF, are nearly constant for all the 5 cycles tested in this study (Figure 6). On comparison of XRD patterns of fresh and used H-Beta catalyst, it can be observed that the exposure of the catalyst to reaction conditions does not result in significant change in the crystal structure (Figure 1). The comparison of FETEM micrographs of fresh and spent H-Beta catalysts is indicated that there is no carbonaceous material formed during the reaction (Figure S4, SI). The excellent stability of the zeolite could be attributed to higher SAR (360:1) of H-Beta used in this study. The higher SAR gives rise to hydrophobic nature of the zeolite and makes the zeolite framework more stable in water at high temperatures. Similar results in terms of stability are obtained by other researchers.^[21b]

II. CONCLUSION

In summary, high yields of 5-HMF from carbohydrates (fructose, glucose, and cellulose) are obtained over zeolites with high mesoporosity. Among the zeolites tested, H-Beta showed the highest 5-HMF yield of 94% with a fructose conversion of 98% at 180°C for 1 h. The highest selectivities to 5-HMF obtained with the glucose and cellulose substrates are 74% (conversion 62%) and 41% (conversion 98%), respectively, at 180°C. The H-Beta is highly selective to 5-HMF production with negligible concentration of side products (< 3%). The H-Beta showed excellent stability with no signs of deactivation even after 5 cycles of reuse. Finally, this study shows that a zeolite with high mesoporosity and high SAR results in higher yield and excellent stability in 5-HMF direct production from cellulose.

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REFERENCES

- [1] aE. Taarning, C. M. Osmundsen, X. Yang, B. Voss, S. I. Andersen, C. H. Christensen, *Energy & Environmental Science* **2011**, *4*, 793-804; bJ. S. Luterbacher, D. Martin Alonso, J. A. Dumesic, *Green Chemistry* **2014**, *16*, 4816-4838; cC. Chatterjee, F. Pong, A. Sen, *Green Chemistry* **2015**, *17*, 40-71; dM. Besson, P. Gallezot, C. Pinel, *Chemical Reviews* **2014**, *114*, 1827-1870; eA. Corma, S. Iborra, A. Velty, *Chemical Reviews* **2007**, *107*, 2411-2502.
- [2] Y. Zhang, J. Zhang, D. Su, *Journal of Energy Chemistry* **2015**, *24*, 548-551.
- [3] aM. E. Zakrzewska, E. Bogel-Lukasik, R. Bogel-Lukasik, *Chemical Reviews* **2011**, *111*, 397-417; bH. Li, S. Yang, A. Riisager, A. Pandey, R. S. Sangwan, S. Saravanamurugan, R. Luque, *Green Chemistry* **2016**, *18*, 5701-5735.
- [4] H. Li, Z. Fang, R. L. Smith Jr, S. Yang, *Progress in Energy and Combustion Science* **2016**, *55*, 98-194.
- [5] L. Qi, Y. F. Mui, S. W. Lo, M. Y. Lui, G. R. Akien, I. T. Horváth, *ACS Catalysis* **2014**, *4*, 1470-1477.
- [6] E. Nikolla, Y. Román-Leshkov, M. Moliner, M. E. Davis, *ACS Catalysis* **2011**, *1*, 408-410.
- [7] S. Jia, K. Liu, Z. Xu, P. Yan, W. Xu, X. Liu, Z. C. Zhang, *Catalysis Today* **2014**, *234*, 83-90.
- [8] H. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, *Science* **2007**, *316*, 1597-1600.
- [9] L. Zhang, H. Yu, P. Wang, *Bioresource Technology* **2013**, *136*, 515-521.
- [10] I. Agirrezabal-Telleria, I. Gandarias, P. L. Arias, *Catalysis Today* **2014**, *234*, 42-58.
- [11] L. Hu, Z. Wu, J. Xu, Y. Sun, L. Lin, S. Liu, *Chemical Engineering Journal* **2014**, *244*, 137-144.
- [12] R. Otomo, T. Yokoi, J. N. Kondo, T. Tatsumi, *Applied Catalysis A: General* **2014**, *470*, 318-326.
- [13] aZ. Zhang, J. Song, B. Han, *Chemical Reviews* **2017**, *117*, 6834-6880; bF. Shahangi, A. Najafi Chermahini, M. Saraji, *Journal of Energy Chemistry* **2018**, *27*, 769-780.
- [14] aM. Moreno-Recio, I. Jiménez-Morales, P. L. Arias, J. Santamaría-González, P. Maireles-Torres, *ChemistrySelect* **2017**, *2*, 2444-2451; bW. Mamo, Y. Chebude, C. Marquez-Alvarez, I. Diaz, E. Sastre, *Catalysis Science & Technology* **2016**, *6*, 2766-2774.
- [15] aS. Kulawong, S. Prayoonpokarach, F. Roessner, J. Wittayakun, *Química Nova* **2015**, *38*, 191-195; bR. Srivastava, B. Sarmah, B. Satpati, *RSC Advances* **2015**, *5*, 25998-26006; cE. Dumitriu, V. Hulea, *Journal of Catalysis* **2003**, *218*, 249-257.
- [16] R. Lobo, *AIChE Journal* **2008**, *54*, 1402-1409.
- [17] C. Wang, L. Zhang, T. Zhou, J. Chen, F. Xu, *Scientific reports* **2017**, *7*, 40908.
- [18] aM. Moreno-Recio, J. Santamaría-González, P. Maireles-Torres, *Chemical Engineering Journal* **2016**, *303*, 22-30; bK. Y. Nandiwale, N. D. Galande, P. Thakur, S. D. Sawant, V. P. Zambre, V. V. Bokade, *ACS Sustainable Chemistry & Engineering* **2014**, *2*, 1928-1932. Y. Roman-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature* **2007**, *447*, 982-985.
- [19] aS. K. Tyrlik, D. Szerszen, M. Olejnik, W. Danikiewicz, *Journal of Molecular Catalysis A: Chemical* **1996**, *106*, 223-233; bE. Combs, B. Cinlar, Y. Pagan-Torres, J. A. Dumesic, B. H. Shanks, *Catalysis Communications* **2013**, *30*, 1-4; cY. J. Pagan-Torres, T. Wang, J. M. R. Gallo, B. H. Shanks, J. A. Dumesic, *ACS Catalysis* **2012**, *2*, 930-934.
- [20] Y. Yang, X. Xiang, D. Tong, C. Hu, M. M. Abu-Omar, *Bioresource Technology* **2012**, *116*, 302-306.
- [21] P. Lanzafame, D. M. Temi, S. Perathoner, A. N. Spadaro, G. Centi, *Catalysis Today* **2012**, *179*, 178-184.
- [22] C. A. Emeis, *Journal of Catalysis* **1993**, *141*, 347-354.
- [23] P. Saxena, B. Velaga, N. R. Peela, *ChemistrySelect* **2017**, *2*, 10379-10386.
- [24] C. Cai, Q. Liu, J. Tan, T. Wang, Q. Zhang, L. Ma, *Conversion of Cellulose to 5-Hydroxymethylfurfural using Inorganic Acidic Catalysts in the Presence of Pressurized Water Steam, Vol. 12*, **2017**.

Supporting Information**Efficient Conversion of Carbohydrates to 5 Hydroxymethylfurfural over Mesoporous Zeolites**

Santosh Kumar Yedla, Animes Kumar Golder and Nageswara Rao Peela

Table S1: Detailed experimental conditions used in this study

Expt no	Temp (°C) & Time (h)	Substrate	Catalyst	Reaction phase composition in 2g of water			Extract ion phase MIB K (g)
				NaCl (g)	Catalyst (g)	Substrate (g)	
1	180, 1.5	Glucose	H-ZSM5	0.6	0.0667	0.2	4
2	180, 2	Glucose	H-ZSM5	0.6	0.0667	0.2	4
3	180, 2.5	Glucose	H-ZSM5	0.6	0.0667	0.2	4
4	180, 3	Glucose	H-ZSM5	0.6	0.0667	0.2	4
5	160, 2	Glucose	H-ZSM5	0.6	0.0667	0.2	4
6	170, 2	Glucose	H-ZSM5	0.6	0.0667	0.2	4
7	180, 2	Glucose	H-Beta	0.6	0.0667	0.2	4
8	180, 2	Glucose	H-MOR	0.6	0.0667	0.2	4
9	180, 2	Glucose	H-Y	0.6	0.0667	0.2	4
10	180, 2	Glucose	H-Beta	0	0.0667	0.2	4
11	180, 2	Glucose	H-Beta	0	0.0667	0.2	0
12	180, 2	Glucose	H-Beta	0.6	0.0667	0.2	0
13	180, 1	Fructose	H-Beta	0.6	0.0667	0.2	4
14	180, 2	Cellulose	H-Beta	0.6	0.0667	0.2	4
15	180, 3	Cellulose	H-Beta	0.6	0.0667	0.2	4
16	180, 4	Cellulose	H-Beta	0.6	0.0667	0.2	4
17	180, 3	Cellulose	H-Beta-R2	0.6	0.0667	0.2	4
18	180, 3	Cellulose	H-Beta-R3	0.6	0.0667	0.2	4
19	180, 3	Cellulose	H-Beta-R4	0.6	0.0667	0.2	4
20	180, 3	Cellulose	H-Beta-R5	0.6	0.0667	0.2	4

Table S2: Selectivity to 5-HMF

Experiment No	Conversion (%)	Selectivity (%)
1	64.3	65.7
2	71.4	63.8
3	90.7	42.3
4	96.2	35.3
5	16.4	70.6
6	32.0	85.1
7	62.4	73.6
8	95.5	37.2
9	72.1	58.2
10	23.8	68.4
11	6.9	72.0
12	62.7	42.2
13	99.8	92.6
14	98.7	35.8
15	98.2	40.5
16	93.9	37.8
17	96.2	44.5
18	97.7	45.3
19	95.7	46.9
20	93.5	48.8

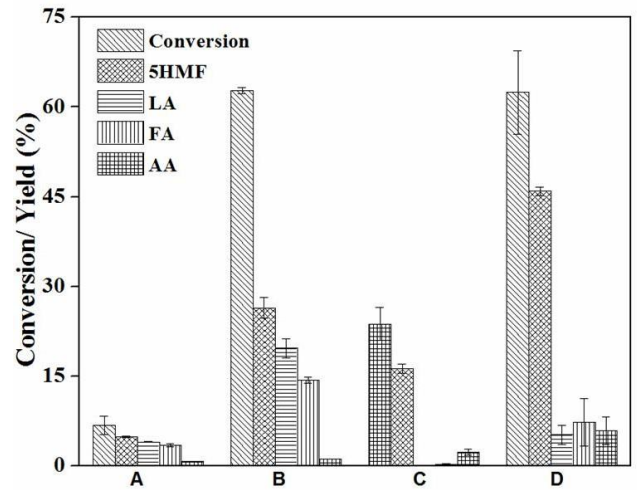
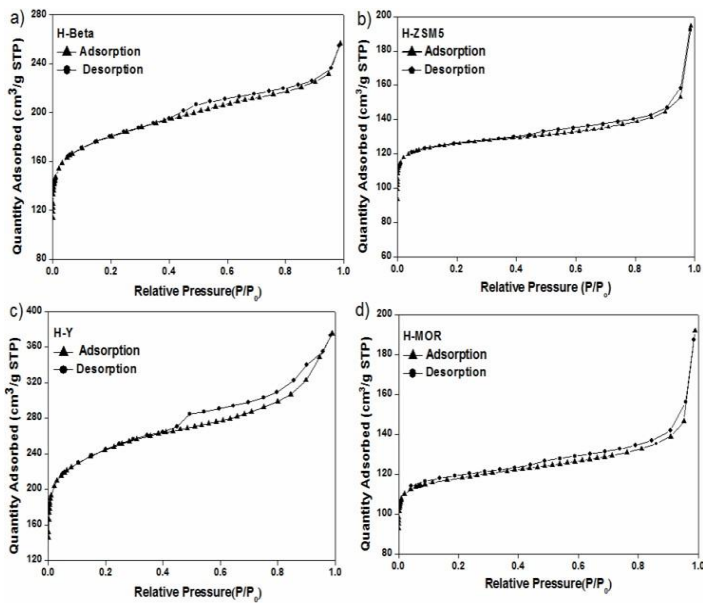


Figure S1: N₂ adsorption – desorption isotherms: (a) H-Beta, (b) H-ZSM5, (c) H-Y, (d) H-MOR

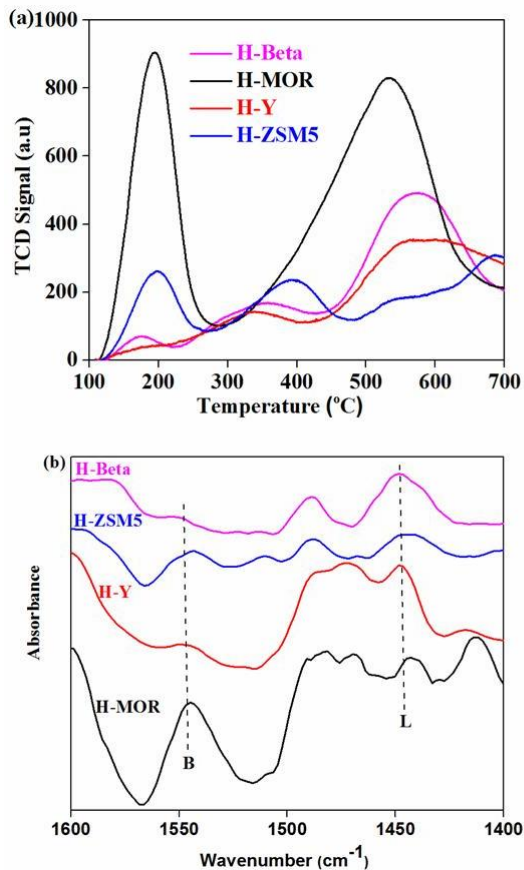


Figure S2: Acidity measurements by NH₃-TPD (a) and Pyridin-FTIR (b), of zeolites H-Beta, H-MOR, H-Y and H-ZSM5.

Figure S3: Conversion of glucose and yield reaction products (5-HMF, LA, FA, and fructose) without (A) and with (B) NaCl in a single phase system; without (C) and with (D) NaCl in a biphasic system; at 180°C and 2 h reaction time.

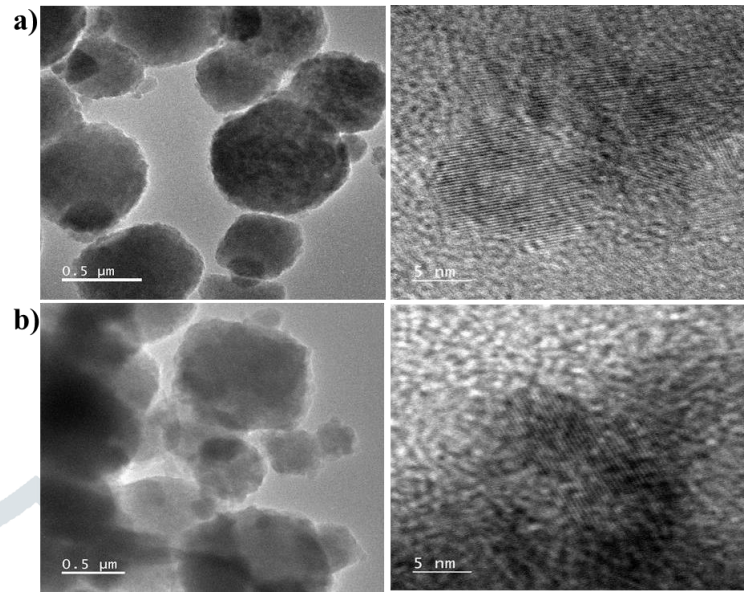


Figure S4: FETEM images of (a) fresh and (b) recycled H-Beta catalyst

