

One-Pot Synthesis of 5-Hydroxymethylfurfural by Cellulose Hydrolysis over Highly Active Bimodal Micro/Mesoporous H-ZSM-5 Catalyst

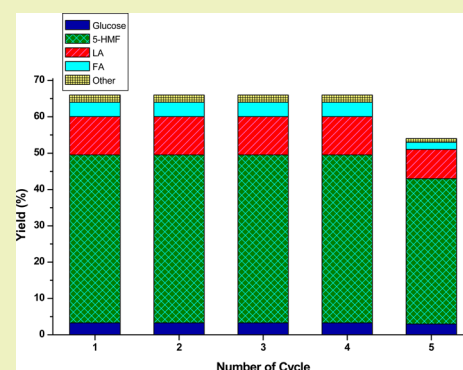
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ABSTRACT: Direct synthesis of 5-hydroxymethylfurfural (5-HMF), a useful renewable biofuel and biochemical, was systematically studied by hydrolysis of microcrystalline cellulose over Bimodal-HZ-5 zeolite. Bimodal-HZ-5 zeolite obtained by post-synthesis modification of H-ZSM-5 with desilication was found to be a potential heterogeneous catalyst with 67% cellulose conversion and 46% yield of 5-HMF. Bimodal-HZ-5 was observed to be reusable for four cycles, without any loss in activity. The detailed optimization of process parameters and catalyst reusability are also presented. The present study opens a new avenue for the renewable one-pot synthesis of 5-HMF, a valuable product.



KEYWORDS: Microcrystalline cellulose, Hydrolysis, Bimodal-HZ-5, Glucose, 5-Hydroxymethylfurfural

INTRODUCTION

Research on conversion of renewable resources to green chemicals has drawn much attention over the past decade. The lingo-cellulosic biomass-like agricultural residues and wood chips contain C₆-sugars (e.g., D-fructose, D-glucose, and D-mannose), which are valuable precursors for numerous chemicals having valuable applications.^{1,2} The target molecules include organic acids such as formic acid (FA), levulinic acid (LA), and furanics like 2,5-dimethylfuran and 5-hydroxymethylfurfural (5-HMF). Of these, particularly 5-HMF is currently receiving a great deal of attention. 5-HMF can be converted to a range of derivatives having potential applications in the biofuels (furanics), polymer, and solvent industries.

5-HMF is synthesized by hydrolysis of C₆-sugars in water over acid catalysts.³ Conventionally, inorganic acids such as hydrochloric acid and sulfuric acid have been used. Best results were reported with D-fructose and HCl, whereas inferior results were obtained for D-glucose.^{4,5} These homogeneous catalysts have major problems in catalyst recycle, reactor, and equipment corrosion, product separation, etc. In contrast, solid acid catalysts have numerous advantages over liquid catalysts regarding activity, selectivity, catalyst life, ease in recovery, and reuse. In this context, recently, various solid acid catalysts such as heteropoly acid,⁶ sulfonated resins,⁷ sulfonated carbon,⁸ sulfonic acid functionalized silica,⁹ WO₃/ZrO₂,¹⁰ Ru/CMK,¹¹ ionic liquids,^{12,13} zirconium phosphate,¹⁴ hierarchical H-USY zeolites,¹⁵ sulfonated hierarchical H-USY zeolite,¹⁶ TiO₂,¹⁷

SO₄²⁻/Ti-MCM-41,¹⁸ and hot compressed steam with the aid of dihydric phosphates¹⁹ have been tested for hemicellulose and/or cellulose hydrolysis. Yang et al.²⁰ tested solid acid catalysts such as H-Beta, H-Y, and H-ZSM-5 to obtain HMF from glucose. The HMF yield obtained over large pore zeolite such as H-Beta (9%) and H-Y (9%) was less than that over medium pore zeolite H-ZSM-5 (12%).²⁰ However, it is still a technological challenge to develop ecofriendly and efficient catalytic hydrolysis processes with a heterogeneous acid catalyst because of their limitations such as catalytic activity and acid strength declines in the presence of water.

Hence, present study is devoted to develop a high performance heterogeneous solid catalyst for hydrolysis of cellulose to glucose and other value-added products such as 5-HMF. In the present study, bimodal micro/mesoporous H-ZSM-5 (Bimodal-HZ-5) was synthesized by post-modification of H-ZSM-5 with desilication. Well-characterized Bimodal-HZ-5 was used for the one-pot synthesis of 5-HMF by cellulose hydrolysis, probably for the first time. The detailed optimization of process parameters and catalyst reusability are also presented.

Received: April 21, 2014

Revised: June 2, 2014

Published: June 16, 2014

Table 1. Characterization of Catalysts

catalyst sample	Si/Al ratio	BET surface area (m ² g ⁻¹)	pore volume (cm ³ g ⁻¹)			B/L ratio	total acidity (mmol g ⁻¹)	relative crystallinity (%)
			meso	micro	total			
H-ZSM-5	37.00	300.8	—	—	0.220	0.641	0.51	100
Bimodal-HZ-5	30.15	427.6	0.128	0.190	0.318	0.817	0.73	97

MATERIALS

The microcrystalline cellulose powder (99% purity) and HPLC grade acetonitrile were purchased from m/s Sigma-Aldrich, U.S.A. NaOH and ammonium nitrate were obtained from M/s Loba Chemie, Mumbai, India. HPLC methanol was procured from Merck Chemicals, India.

Catalyst Synthesis and Characterization. The protonic form H-ZSM-5 with Si/Al ratio 37 was synthesized as per the reported procedure.²¹ The bimodal micro/mesoporous H-ZSM-5 (Bimodal-HZ-5) was obtained by mixing 0.2 M aq. NaOH with H-ZSM-5 (in the proportion of 30 mL g⁻¹) and kept at 338 K for 30 min.²² Then sample was subjected to 3-fold ion exchange with aq. 0.1 M ammonium nitrate (in the proportion of 10 mL g⁻¹ of product for 5 h). Finally, samples were transformed into the hydrogen forms by calcinations in air at 823 K for 5 h.

Detailed characterizations for H-ZSM-5 (parent) and Bimodal-HZ-5 (with designation as DH-ZSM-5₉₇) catalyst samples can be found in our previous publication.²² Energy dispersive X-ray analysis (EDAX) was used to determine the Si/Al ratio of the synthesized catalysts (Table 1). X-ray diffractometer (P Analytical PXRD system, Model X-Pert PRO-1712) with Cu K α radiation at a scanning rate of 0.0671 s⁻¹ in the 2 θ range of 10–50 (degree) was utilized to identify phase purity and degree of crystallization of synthesized catalysts (Figure 1a). Nitrogen adsorption and desorption isotherms at 77 K were obtained with a SA 3100 analyzer (Beckman Coulter, CA, U.S.A.). The specific surface area of synthesized catalysts was calculated using the Brunauer–Emmett–Teller (BET) method (Table 1). Temperature-programmed ammonia desorption (TPAD) coupled to Micromeritics AutoChem (2910, U.S.A.) equipped with a thermal conductivity detector was used to measure the total acidity of catalyst samples (Table 1). The Brönsted to Lewis acid ratio (B/L ratio) of the catalyst sample was determined by ex-situ FTIR spectroscopy with chemisorbed pyridine (Table 1). The synthesized catalyst samples were activated at 673 K for 2 h. High vacuum was used to cool the samples to room temperature. Then the samples were subjected to pyridine vapors for 2 h. The samples were treated at 423 K for 2 h to drive off physisorbed pyridine. A Shimadzu (Model-820 PC) spectrophotometer under DRIFT (diffuse reflectance infrared Fourier transform) mode was used to record FTIR spectra of catalyst samples (Figure 1b).

Catalytic Evaluation and analysis. The catalytic hydrolysis of cellulose was carried out in 100 mL cylindrical stainless steel batch reactor. The desired quantity of cellulose (0.25 g), distilled water (5–20 mL), and catalyst (0.15–0.75 g) were introduced into the autoclave. The reactions were performed at temperature of 443–473 K for 4 h. The unreacted cellulose and the catalyst were separated by filtration. After filtration, the amount of unreacted cellulose was calculated by deducting the catalyst weight from recovered solid. Conversion of cellulose was obtained by the difference in weight of cellulose before and after the reaction, with an experimental error of $\pm 2\%$. The liquid reaction products were analyzed by using a HPLC, Jasco, PU-2089 (4.6 mm \times 250 mm) column, equipped with a quaternary pump and photo diode array (PDA) detector. A PDA detector was used to detect products such as glucose, 5-HMF, LA, and FA. The mobile phase was set at 80:20 v/v acetonitrile:water (pH 8.2) at a total flow rate of 1 mL min⁻¹. The products were quantified by an external standard method based on the average peak area of each product under three parallel HPLC measurements of each experiment. The concentrations of glucose, 5-HMF, LA, and FA were calculated based on the standard curve obtained using an authentic samples. The analytical errors for glucose, 5-HMF, LA, and FA yields were evaluated to be within the range of $\pm 2\%$. The selectivity and yield of the desired products were calculated from following equations

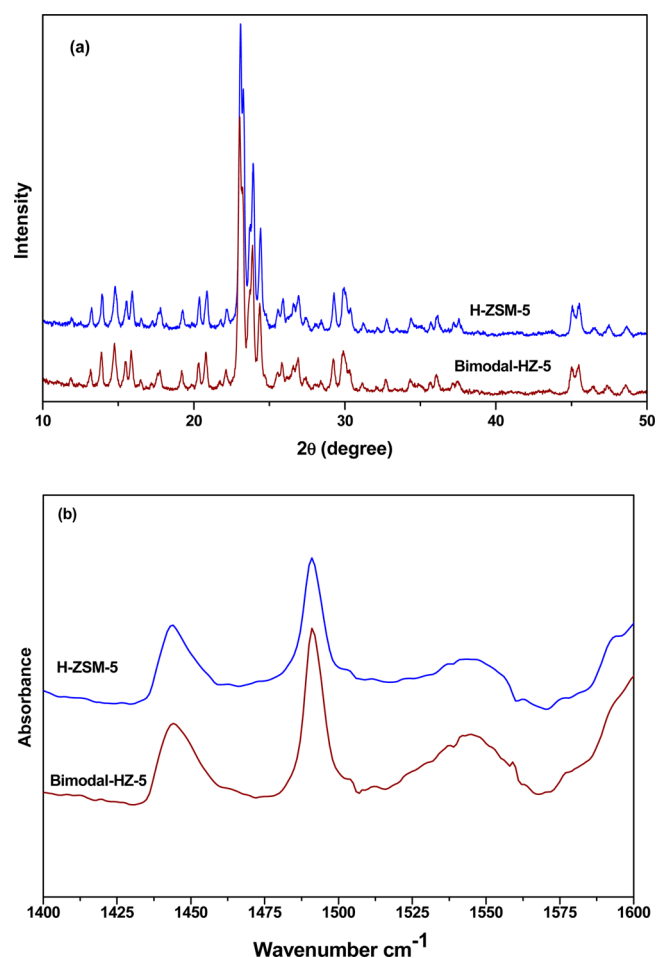


Figure 1. Characterization of H-ZSM-5 and Bimodal-HZ-5 catalyst: (a) Powder X-ray diffraction (XRD) patterns. (b) Pyridine FTIR spectra.

$$\text{selectivity (\%)} = \frac{\text{(concentration of desired product)}}{\text{(concentration of total products)}} \times 100$$

$$\text{yield (\%)} = (\% \text{cellulose conversion}) \times (\% \text{selectivity of desired product}) / 100$$

RESULTS AND DISCUSSION

Physico-Chemical Properties of Catalysts. The XRD pattern of H-ZSM-5 showed a fully crystalline (100%) zeolite phase and that of Bimodal-HZ-5 was observed to be of 97% relative crystalline without the impurity phase (Figure 1a). This is attributed to removal of Si from the framework of the zeolite by the NaOH treatment, but basic fingerprints of zeolite were maintained.²² The pyridine-FTIR spectra of the H-ZSM-5 and Bimodal-HZ-5 samples exhibited bands at 1445, 1545, and 1490 cm⁻¹ and are attributed to Lewis (L), Brönsted (B), and B and L acid sites, respectively (Figure 1b).²² An intensity in both

bands (B and L) was observed to increase in Bimodal-HZ-5 as compared to H-ZSM-5. Physico-chemical properties of synthesized catalysts are presented in Table 1. EDAX analysis revealed that Bimodal-HZ-5 has a lower Si/Al ratio as compared to parent H-ZSM-5, which confirms the removal of Si from the zeolitic framework due to alkali treatment (Table 1). Bimodal-HZ-5 exhibited an increase in its BET surface area, which is due to the significant increase in the mesopore surface area and volume. The higher B/L ratio and higher total acidity of Bimodal-HZ-5 in comparison with parent H-ZSM-5 is attributed to a decrease in the Si/Al ratio (Table 1).

Performance of Catalysts in Cellulose Degradation.

Catalytic degradation of cellulose over Thermal (without catalyst), H-ZSM-5, and Bimodal-HZ-5 at identical process parameters is presented in Figure 2. The overall trend of

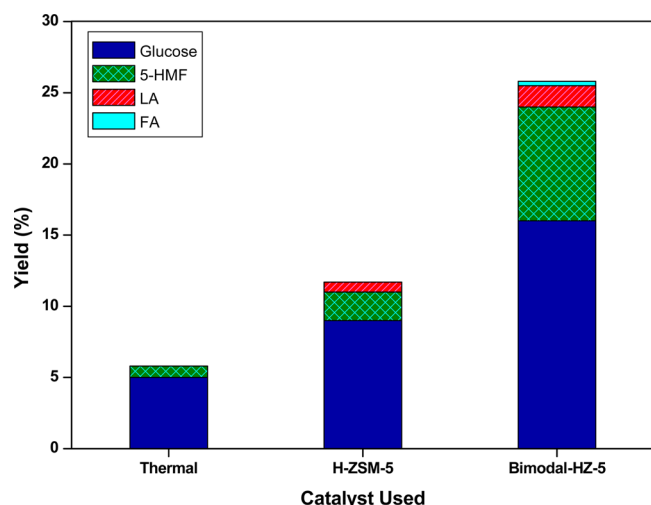


Figure 2. Catalytic hydrolysis of cellulose over Thermal, H-ZSM-5, and Bimodal-HZ-5 at process parameters of microcrystalline cellulose = 0.25 g, water = 10 mL, catalyst = 0.25 g, reaction temperature = 443 K, and reaction time = 4 h.

cellulose conversion followed Bimodal-HZ-5 (26%) > H-ZSM-5 (11%) > Thermal (6%). The increase in formation of glucose was observed in all cases, and the highest glucose formation of 16% was noticed with Bimodal-HZ-5. Also, the yield of 5-HMF over Bimodal-HZ-5 (8%) was higher than that of H-ZSM-5 (2%). The higher cellulose conversion and higher yield of glucose and 5-HMF over Bimodal-HZ-5 than H-ZSM-5 is attributed to an increase in BET surface area, total pore volume, B/L ratio, and total acidity. Also, the lower Si/Al ratio of Bimodal-HZ-5 in comparison with H-ZSM-5 tends to increase Brønsted acid sites and contributes toward higher activity.

Bimodal-HZ-5 was found to be a potential catalyst with 26% cellulose conversion and 16% glucose and 8% 5-HMF yields, respectively. The effect of various process parameters on cellulose hydrolysis over Bimodal-HZ-5 were investigated in view to maximize the yield of 5-HMF.

Optimization of Process Parameters. Effect of Water

Quantity. The amount of water is an important parameter for the cellulose hydrolysis;¹³ hence, content of water was varied from 5 to 20 mL at identical process parameters to access its effect on cellulose conversion and 5-HMF yield (Figure 3). As the quantity of water increased from 5 to 10 mL, the cellulose conversion was found to increase from 14% to 26%. With a further increase in the quantity of water above 10 mL, a

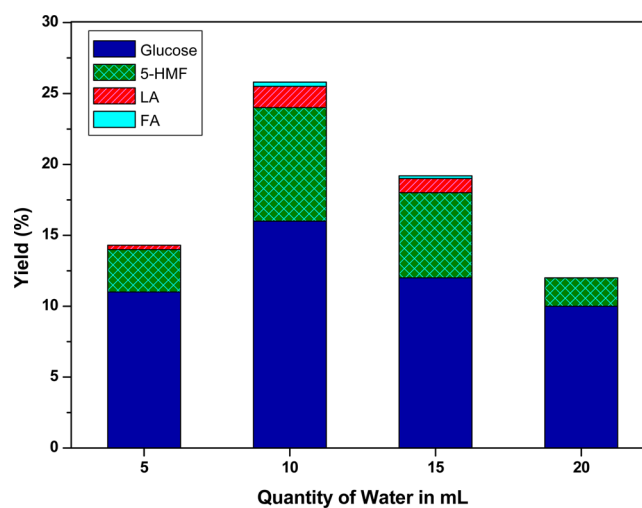


Figure 3. Effect of water quantity on cellulose hydrolysis over Bimodal-HZ-5 catalyst at process parameters of microcrystalline cellulose = 0.25 g, catalyst = 0.25 g, reaction temperature = 443 K, and reaction time = 4 h.

decrease in cellulose conversion was observed. Excess water, given more dilution to solid cellulose affects its further solubility and accessibility with active acids sites on catalyst surface, led to a reduction in the rate of hydrolysis. Hence, 10 mL of water quantity with 16% glucose yield and 8% yield of 5-HMF along with 1.5% LA yield was selected as an optimum water quantity, and the same was used in further experiments.

Effect of Catalyst Weight. The effect of different catalyst weights of Bimodal-HZ-5 on cellulose conversion and 5-HMF yield was studied in the range of 0.15–0.75 g (Figure 4). Figure

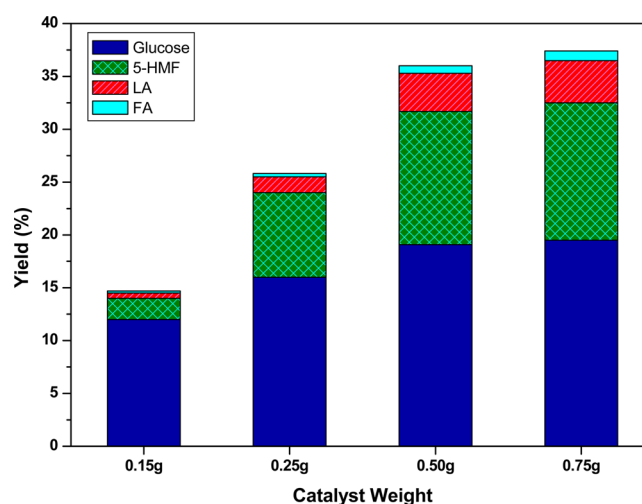


Figure 4. Effect of catalyst weight on cellulose hydrolysis over Bimodal-HZ-5 catalyst at process parameters of microcrystalline cellulose = 0.25 g, water = 10 mL, reaction temperature = 443 K, and reaction time = 4 h.

4 indicates that the overall cellulose conversion increased rapidly from 15% to 36% with an increase in the weight of catalyst from 0.15 to 0.50 g. In this range, the yield of glucose and 5-HMF were also found to increase from 12% to 19% and 2% to 13%, respectively. More catalyst means more active acid sites, which increases the rate of cellulose hydrolysis. However, only a fair increase in cellulose conversion was obtained with an

increase in the amount of catalyst from 0.50 to 0.75 g. This may be reasoned that a large amount catalyst provides more catalyst active sites than required by the reactant molecules. Thus, the excess catalyst caused the side reactions such as polymerization and rehydration of the products leading to excess formation of LA (0.5–4%) and FA (0.2–1%). Therefore, in the present study, 0.50 g of catalyst would be optimum and an appropriate amount at the studied reaction conditions.

Effect of Temperature. The cellulose hydrolysis reactions were carried out at four different temperatures in the range of 443 to 473 K. As shown in Figure 5, the reaction temperature

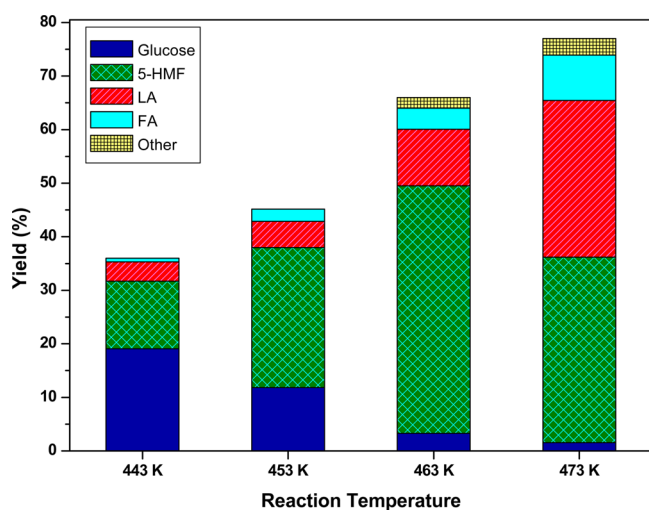


Figure 5. Effect of temperature on cellulose hydrolysis over Bimodal-HZ-5 catalyst at process parameters of microcrystalline cellulose = 0.25 g, water = 10 mL, catalyst = 0.50 g, and reaction time = 4 h.

has a significant influence on cellulose conversion and yield of 5-HMF. As the reaction temperature increased from 443 to 473 K, the cellulose conversion increased from 37% to 77%. This may be due to an increase in temperature (443–473 K) leading to an increase in the rate of cellulose depolymerization to glucose. The dehydration of glucose was found to be accelerated by increasing the temperature (443–463 K), which was favorable to obtain a high yield of 5-HMF (13–46%). With a further increase in temperature from 463 to 473 K, the yield of 5-HMF decreased to 35%. This is attributed to an increase in the rate of rehydration and polymerization of 5-HMF at a higher reaction temperature to LA and FA or humins formation. This is also supported by a sharp increase in yield of LA from 11% to 29% within the temperature range of 463–473 K. Formic acid showed an increase in yield from 1% to 8% with an increase in temperature from 443 to 473 K. At higher reaction temperatures of 463 and 473 K, 2–3% of other byproducts were obtained. This may be due to rehydration of LA and FA, other side reactions, or humins production. The reaction temperature of 463 K was found to be optimum with 67% cellulose conversion and 46% yield of 5-HMF.

Reusability of Catalyst. The recyclability of the catalyst is of great importance to making the production of 5-HMF industrially benign. The reusability of Bimodal-HZ-5 catalyst was investigated at optimized process parameters of 0.25 g of microcrystalline cellulose, 10 mL of water, 0.50 g of catalyst, 463 K of reaction temperature, and 4 h of reaction time. After completion of each reaction, the catalyst and unreacted cellulose were separated by filtration. The catalyst sample

obtained after each reaction was used without any post-treatment. During each cycle, fresh cellulose was added to make up the cellulose weight. It is shown in Figure 6 that Bimodal-

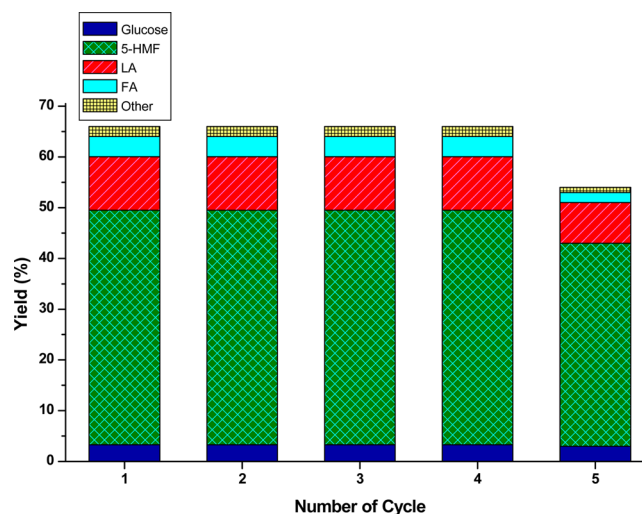


Figure 6. Reusability of Bimodal-HZ-5 catalyst in hydrolysis of cellulose at process parameters of microcrystalline cellulose = 0.25 g, water = 10 mL, catalyst = 0.50 g, reaction temperature = 463 K, and reaction time = 4 h.

HZ-5 catalyst was stable for four catalytic cycles with 67% cellulose conversion and 46% yield of 5-HMF. For the fifth cycle, a decrease in cellulose conversion (67–54%) and yield of 5-HMF (46–40%) were observed.

Chareonlimkun and co-workers reported a 27% HMF yield using TiO_2 from its chloride precursor.¹⁷ Recently, Jiang et al.¹⁸ obtained about a 13–18% HMF yield over the $\text{SO}_4^{2-}/\text{Ti-MCM-41}$ catalyst, and Shi et al.¹⁹ were able to obtain a 34 mol % of HMF yield from cellulose degradation in hot compressed steam with the aid of dihydric phosphates. Thus, a 46% 5-HMF yield obtained in the present study is higher than in the reported literature.

This study demonstrates the principles of green chemistry such as a safe synthetic method, reusable heterogeneous catalyst, ambient operating parameters, and minimized material diversity (high selectivity of desired product). The present method of using Bimodal-HZ-5 catalyst for cellulose hydrolysis to produce 5-HMF directly offers principles of green chemistry and engineering and with potential benefits with respect to high cellulose conversion (67%), high yield of 5-HMF (46%), and better reusability of catalyst for a minimum of four catalytic cycles without considerable loss in activity (Figure 6).

CONCLUSIONS

The one-pot catalytic hydrolysis of microcrystalline cellulose to glucose and 5-HMF over Bimodal-HZ-5 was systematically studied. Bimodal-HZ-5 was prepared by post-modification of H-ZSM-5 by desilication. Bimodal-HZ-5 has shown improvement in total surface area, total pore volume, and total acidity as compared to parent H-ZSM-5. The maximum cellulose conversions of 67% and 46% yields of 5-HMF and <5% glucose formation were obtained over the Bimodal-HZ-5 catalyst, at optimized process parameters. Bimodal-HZ-5 was observed to be stable for four catalytic cycles. The high cellulose conversion and direct formation of 5-HMF (46%)

make the process clean, renewable, and economical following maximum principles of green chemistry and engineering.

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Notes

The authors declare no competing financial interest.

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