Valorization of Microcrystalline Cellulose using Heterogeneous Protonated Zeolite Catalyst: An experimental and kinetics approach

Samuel Kassaye
Kansas State University
Dinesh Gupta
Indian Institute of Technology
Kamal. K. Pant
Indian Institute of Technology Delhi
Sapna Jain (sjain@alasu.edu)
Alabama State University https://orcid.org/0000-0002-0164-1446

Research Article

Keywords: Microcrystalline cellulose, Ionic liquid, Hydrolysis, Kinetic modelling

Posted Date: April 14th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-381188/v1

Valorization of Microcrystalline Cellulose using Heterogeneous Protonated Zeolite Catalyst: An experimental and kinetics approach

Samuel Kassaye[1], Dinesh Gupta[1], Kamal. K. Pant[1], Sapna Jain*[2]

[1]Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India

[2]Department of Physical Science, Alabama State University, Montgomery Al 36104, USA

*Author for correspondence: Tel.: 334-467-7083
*E-mail address: sjain@alasu.edu (Sapna Jain)

Abstract

This study aims to valorize microcrystalline cellulose (MCC) using protonated zeolite catalysts such as (H-ZSM-5) and Cr/H-ZSM-5 (5 %) in ionic liquid. The catalytic effect in synergy with 1-butyl-3-methylimidazolium Chloride ([BMIM] Cl) ionic liquid was studied in detail. The total reducing sugar (TRS) was determined using 3, 5-dinitrisalcylic acid (DNS) array method. The catalysts were characterized using techniques such as Fourier transform infrared (FT-IR), X-ray diffraction analysis (XRD), temperature-programmed desorption of ammonia (NH_3-TPD), and BET-surface area analyzer. H-ZSM-5 effectively depolymerized cellulose with a maximum yield of 70% total reducing sugar (34% glucose, 8% fructose, and 4.5% 5-HMF) Cr/H-ZSM-5 catalyst dehydrates fructose to 5-HMF with a yield of 53%. The use of ionic liquid significantly reduced the activation energy of formation and decomposition. The activation energy determined in cellulose hydrolysis was 85.83 KJ mol^{-1} for a reaction time of 180 min while the decomposition energy was found to be 42.5 kJ mol^{-1}.

Keywords: Microcrystalline cellulose, Ionic liquid, Hydrolysis, Kinetic modelling

1. Introduction

Efficient and Economic conversion of lignocellulosic biomass (LCB) to value-added chemicals in integrated biorefinery is believed to reduce the dependency on a nonrenewable resource such as fossil fuel. LCB is a promising feedstock for the biorefinery industry to produce biofuel and valuable chemicals from renewable sources [1]. Successful utilization of biomass demands the effective conversion of the cellulosic portion of LCB to develop integrated biorefinery to produce biofuel and chemicals economically. The hydrolysis of cellulose strongly depends on its properties such as degree of polymerization and crystallinity. The utilization of lignocellulosic biomass depends on the level of success achieved on hydrolysis of the cellulose into its monomeric form, glucose [2]. However, cellulose is the most recalcitrant and well-known crystalline biopolymer due to its extensive intra and inter-hydrogen bonding network. Cellulose is a structurally linear polymer composed of glucose monomers joined together by β-1, 4-glycosidic linkage [3]. Therefore, it is difficult to dissolve and subsequently hydrolyze cellulose using conventional organic solvents including water and ethanol [4] [5].

The hydrolysis of cellulosic biomass is carried out using an enzymatic approach accompanied by a high glucose yield at moderate reaction conditions. Enzymatic hydrolysis has several disadvantages related to the high cost of enzymes, limited cellulose conversion, and scalability challenges [3]. Hydrolysis of cellulose using acidic catalysts such as liquid acids including mineral and organic acids is another alternative option [6]. Mineral acids are highly efficient in breaking β-1,4-glucosidic linkage [7] [8]. However, this method has several drawbacks: reaction product decomposition, difficulty in the product, and catalyst separation. Mineral acid catalysts are also known to cause reactor corrosion, costly post- treatment, challenges in recycling catalysts and consumption of a large amount of neutralizing agents [9] [10]. As a result, attempts are underway

to apply solid acid catalysts to convert lignocellulosic biomass to bio-chemicals. The application of ionic liquids further improves this approach. Some selected ionic liquids have inherent characteristics to dissolve cellulose and disrupt the hydrogen bonding network effectively.

Ionic liquids (ILs) are low melting point organic salts that can be utilized both as solvents and catalysts to convert lignocellulosic biomass [11]. The suitability of ILs for biomass utilization is attributed mainly to their tunable Physico-chemical properties such as viscosity, polarity, and thermal stability. ILs act as non-volatile polar solvents and it can dissolve the complex cellulosic materials. The use of ILs allows production flexibility with high efficiency while eliminating the use of undesirable volatile solvents. In this regard, solid acid catalysts such as zeolites, ion exchange resins, and zirconia are considered an alternative chemo-catalytic approach for cellulose depolymerization. The use of zeolite based solid acid catalysts have tremendous advantages compared to homogeneous catalysts such as easy separation, recyclability, and adjustable surface acidity [12].

Zeolite catalysts have been modified and used in industrial processes as milestones in history and have brought profound changes in the petrochemicals industry. For example, Zeolite Y's use in the Fluid Catalytic Cracking (FCC) process significantly increased fuel production efficiency. HZSM-5, which has 8 to 10-member ring with pore-size between 0.5 and 56 nm, is well suited for bio-refinery. However, cellulose insolubility in aqueous media has been the foremost hurdle to apply zeolites as solid acid catalysts due to solid-solid formation which limits mass transfer and reactivitiy. However, ionic liquids with unique properties to dissolve cellulose and reduce its crystallinity have been a choice to convert cellulose to value-added chemicals [13] [14].

Zeolites inherently possess both Bronsted and Lowry as well as Lewis acid sites. These acidic sites help catalyze and promote hydrolysis of cellulose, isomerization of glucose, and fructose dehydration [15]. H-ZSM-5 catalyst has been the choice of this study due to its inherent properties,

such as strong and active acid sites suitable for a catalyst with a porous structure and larger surface area. These properties enhance and facilitates the depolymerization of cellulose to produce bio-chemicals. In this research work, the catalytic effects of H-ZSM-5 and Cr/H-ZSM-5 (5 %) were studied to depolymerize MCC. The experimental results showed that the synergy between ionic liquid and H-ZSM-5 improved cellulose conversion and the yield of the desired bio-chemicals. Results showed that this approach generated a 70% yield of total reducing sugar (34% glucose, 8% fructose and 4.5% 5-HMF) at moderate temperature and atmospheric pressure. Besides, ionic liquid presence significantly reduced the activation energy of the formation and decomposition of sugar.

2. Materials and Methods

2.1 Materials

All the chemicals used were of analytical grade (purity 99.9%). Microcrystalline cellulose extra pure, the average particle size of 90μm is purchased from Alfa Aesar (A Johnson Matthey Company, Heysham, Lancashire, United Kingdom). As reported in our previous research work [16], the original MCC's initial crystallinity index was found to be 76%, which reduced to 42% due to the influence of the ionic liquid. 1-Chlorobutane, N-methyl imidazole, toluene, acetone acetonitrile, ethyl acetate, 3,5-dinitrisalcylic acid, sodium hydroxide, sodium potassium tartrate phenol, acetonitrile, cellulose and isopropanol were purchased from Fisher Scientific (Anand Bhuvan, Princess Street Mumbai, India), H-ZSM-5 with Si/Al ratio of 30 was obtained from Sud-chemie India. [BMIM] Cl ionic liquid was prepared and characterized as reported in our previous work [16].

2.2 Methods

2.2.1 Catalysts Synthesis and Characterization

Chromium-impregnated H-ZSM-5 (Cr/H-ZSM-5) catalyst was prepared using wet impregnation method in which H-ZSM-5 was mixed with chromium precursor ($CrCl_3.6H_2O$) in 50 ml distilled water [17]. The mixture was stirred vigorously for 3 h at 80 ºC and then, the excess solvent was removed by rotary evaporator at reduced pressure. Subsequently, the sample was dried overnight at 120 ºC and calcined at 500 ºC for 5 h. The catalysts were characterized using FTIR, XRD, BET surface area, ammonia TPD and TGA. The thermal properties of both catalysts were studied using thermo-gravimetric analysis (TGA). The analysis was performed using nitrogen gas as a purge gas at a flow rate of 30 ml per min with a heating rate of 20 ºC per min from 30 to 1,000 ºC.

Temperature programmed desorption of ammonia (NH_3-TPD) was performed to determine the total acid strength and acid site distribution on the surface of both catalysts using the Micromeritics Pulse Chemisorb 2720 instrument. The chemisorb instrument is equipped with a quartz reactor and a thermal conductivity detector (T.C.D). The sample catalyst (0.2 g) was pre-treated at 250 ºC for 2h with a continuous flow of pure helium gas to remove the moisture content at room temperature. The sample was then saturated with 10% ammonia gas for adsorption for 1h. After complete saturation, physisorbed ammonia was removed by flowing helium for 30min. The TPD was carried out in a stream of helium gas, raising the temperature from 50º C to 980 ºC at the rate of 10 ºC per min. The desorption process of ammonia was monitored using a T.C.D detector and the amount of total desorbed ammonia was obtained from the integrated peak area of the TPD profiles relative to the calibration curve.

2.2.2 Catalytic Hydrolysis

The hydrolysis of MCC was performed using a batch reactor of 250ml size where the dissolution of MCC was performed in [BMIM] Cl ionic liquid with 1:20 w/w proportion. The stirring was

carried out continuously for 30 min until the mixture turns homogeneous. Then, 5 mL of distilled water and H-ZSM-5 (1:2 w/w ratio of MCC to H-ZSM-5) was added and the solvent was reflexed back to the reactor using a condenser. On the completion of the reaction time, the reaction mixture was quenched using an ice bath. Then, the catalyst and the hydrolysate were separated using vacuum filtration process. The hydrolysate was centrifuged at 10,000 rpm for 10min and then stored in a refrigerator for further analysis.

2.2.3 Hydrolysis Product Analysis

The samples were analyzed using dinitrosalicyclic acid (DNS) reagent in UV-Vis Spectroscopy for TRS yield while HPLC was used to determine the yield of sugars and dehydration products. DNS analysis hydrolysate was mixed with DNS reagent in 1:2 v/v ratio and boiled for 10 minutes in a water bath. The resulting solution was cooled using an ice bath and the analysis was carried out by measuring the absorbance of the sample using UV–Vis spectroscopy (CARY 100Conc) at 540 nm wavelength. The total reducing sugar yield was determined from the calibration curve formed using four-point concentration of standard glucose solutions. The yield of TRS was calculated using Equation 1.

$$\text{TRS Yield } (\%) = \frac{\text{Mass of reducing sugar} \times \frac{162}{180} \times 100}{\text{Mass of dry cellulose}} \quad (1)$$

Fructose, glucose, and 5-HMF were analyzed using high-performance liquid chromatography (HPLC). The HPLC analysis was performed using Agilent technology 1200 infinity equipped with Bio-Rad Aminex HPx-87H 300 x 7.8 mm columns, UV-detector for sugar dehydration product and RI detector for sugar products. The eluent was 5mM sulphuric acid with a flow rate of 0.6 ml per minute and the injection volume was 20 µl. The identification of products in the sample was

performed using a pure form of the products to determine retention time and calibration curve formation. The 5-HMF was calculated as given below in Equation 2.

$$5\text{-HMF Yield}\,(\%) = \frac{\text{moles of 5-HMF produced} \times 100}{\text{moles of cellulose feed}} \quad (2)$$

3. Result and Discussion

3.1 Catalysts Characterization

The catalyst was characterized using FTIR, XRD, BET surface area, ammonia TPD and TGA analysis as discussed below.

3.1.1 FT-IR Analysis

H-ZSM-5 and Cr/H-ZSM-5 catalysts were characterized by FT-IR method to study the effect of chromium metal incorporation into the framework structure of the H-ZSM-5 catalyst. The FTIR spectra of H-ZSM-5 and Cr / H-ZSM-5 catalysts range between 500 and 2000 cm^{-1} shown in Figure 1. The result shows that the position of sensitive structural bands of H-ZSM-5 and Cr/H-ZSM-5 catalysts have similar positions. This implies that chromium metal incorporation into the zeolite structure was insignificant to alter the basic zeolite structure and functional groups. The internal vibrations of SiO_4 and AlO_4 are represented by the absorption bands at 1,088 and 810 cm^{-1}, respectively [18]. Similarly, the bands near 540 and 1225 cm^{-1} are assigned to the double ring vibration and asymmetric stretching.

3.1.2 XRD Analysis

Figure 2 shows the XRD-spectra pattern of H-ZSM-5 and Cr\H-ZSM-5. The XRD data analysis was used to study the effect of chromium metal incorporation on the framework structure of the H-ZSM-5 catalyst. The intensity and the number of diffraction peaks of both catalysts were similar and there is no indication of significant change in the XRD pattern. However, the peak of the Cr/H-ZSM-5 catalyst has shown a slight shift to the left. According to the Bragg equation, this shift in the peak of Cr/H-ZSM-5 catalyst is attributed to the increase in interplanar d-spacing due to chromium metal presence in the framework [19]. This indicates that the bigger lattice parameters representing the inclusion of atoms of different diameters. However, extra diffraction peaks were not observed representing uniform dispersion of chromium throughout the zeolite framework structure [20].

3.1.3 BET Analysis

The BET surface area analysis for H-ZSM-5 and Cr/H-ZSM-5 is given in Table 1. According to the results, the surface area of H-ZSM-5 decreased after the impregnation of chromium metal. Impregnation of chromium metal to H-ZSM-5 led to a decrease in surface area from 270 to 248 m^2g^{-1} due to the partial pores blocking H-ZSM-5 structural support by chromium metal [21].

3.1.4 Ammonia –TPD Analysis

The acid site property of the catalysts was studied using temperature-programmed desorption of ammonia (Ammonia-TPD). As presented in Figure 3, the catalysts' acid site distribution was determined using the desorption peaks. The result showed the effect of chromium metal impregnation into the framework structure on the acidity of H-ZSM-5. The entire surface acid sites of Cr/H-ZSM-5 qualitatively increased compared to H-ZSM-5 implying the presence of additional acid sites due to the inclusion of chromium into the H-ZSM-5 structure [22]. For H-ZSM-5, the

low-temperature peak was observed at a temperature between 150 - 300 ºC while the high-temperature peak was observed in between 300 - 500 ºC representing the low and high desorption peaks, respectively.

Similarly, Cr/H-ZSM-5 catalyst showed the acid sites distribution at a low temperature of 200 - 300 ºC while the high-temperature peak at 350 - 650 ºC. The peak at low and high temperature indicates the presence of weak and strong acid sites, respectively. In general, the incorporation of chromium metal into the frameworks of H-ZSM-5 increased both the strong and the weak acid sites. However, the effect on strong acid sites is more significant than the weak acid sites which are consistent with the literature [21].

3.2 Hydrolysis of MCC

In a preliminary study, hydrolysis of MCC was performed in the absence of H-ZSM-5 catalyst, [BMIM] Cl and prior dissolution for a reference purpose. Compared with the reference, the hydrolysis reaction was significantly influenced by the prior dissolution in ionic liquid and the catalytic amount of H-ZSM-5. In this condition, 70% maximum yield of TRS was achieved at a temperature of 180 oC, reaction time of 180 min, and catalyst to substrate loading ratio of 2:1 (w/w). The high sugar yield from the prior dissolution process is attributed to the structural change from microcrystalline to amorphous cellulose due to the ionic liquid effect [5]. The ionic liquid used was potent enough to break the hydrogen bonding networks which hold the cellulose strand together. As a result, cellulose's crystallinity reduced significantly, facilitating the accessibility of cellulose to the acid sites of the H-ZSM-5 catalyst. The exposure of the acid sites breaks the glycosidic bonds of the glucose monomers. In similar experimental work under identical conditions except for the absence of catalyst, hydrolysis reaction yielded 6% of TRS, exceptionally

low, signifying the catalyst for effective yield. Besides, hydrolysis without prior dissolution resulted in 8% TRS yield. In this case, the low yield of TRS is due to solid-solid interactions of cellulose substrate and H-ZSM-5. Prior dissolution of cellulose decreased the crystallinity and degree of polymerization, which improved the H-ZSM-5 catalyst and the substrate's interaction. In this condition, the dissolved MCC easily migrate to the catalyst's active surface to cause the breakdown of the glycosidic bonds to release the sugar monomers. The higher conversion of cellulose and maximum yield of TRS was obtained due to improved interaction of MCC substrate with the catalyst.

Figure 3 shows, the hydrolysis of MCC and the effect of temperature on the yield of hydrolysis products. The effectiveness of the hydrolysis of MCC in the catalytic effect of H-ZSM-5 in the presence of [BMIM] Cl ionic liquid was studied based on TRS, glucose, fructose and 5-HMF yield. The hydrolysis reaction results at the different temperatures indicated that the maximum yield of TRS was obtained at 180 °C whereas for glucose the maximum yield was obtained at 190 °C. The TRS yield showed an increase as temperature raised from 160 ºC to 180 ºC. However, the yield showed a decreasing trend as temperature further increased due to the decomposition of TRS. As seen in Figure 4, the hydrolysis of MCC is significantly affected by reaction temperature and time. The results implied a maximum of 70% TRS comprising of 34% glucose, 8% fructose and 4.5% 5-HMF at a temperature of 180 °C and hydrolysis time of 180 min. Similarly, the effect of hydrolysis time on the yield of TRS, glucose and fructose at different temperatures showed that the product yield is significantly affected by reaction time. The yield of TRS increased with time and reached a maximum of 180 min of hydrolysis time. Afterward, the TRS yield decreased due to the decomposition of sugars because of extended reaction time. As can be observed from Figure 2, the depolymerization of cellulose using H-ZSM-5 catalyst in [BMIM] Cl ionic liquid results in

an increasing trend and decreases at extended time depolymerization. For cellulose hydrolysis carried out for a run time of 180 min and at a catalyst to substrate ratio of 2:1 resulted in a sharp increase in TRS yield as the temperature increased from 160 ºC (44% yield of TRS) to 180 ºC (70% yield of TRS). However, further raising the temperature from 180 ºC to 200 ºC deceased the yield to 60%. This is caused due to the decomposition of sugars such as glucose and fructose as the temperature is increased above 180ºC for 180 min of hydrolysis time.

For a comparative study, the experiments were carried out in a round bottom flask kept in an oil bath. A typical experimental process is as follows: 0.1 g cellulose is dissolved in 2.0 g [BMIM] Cl at predetermined dissolution temperature and time, and then a catalytic amount of H-ZSM-5 catalyst and 5ml of distilled water was added to the mixture. The Depolymerization of MCC was carried out via two main steps; first through the prior dissolution of MCC in [BMIM] Cl ionic liquid followed by hydrolysis by solid acid catalysts, H-ZSM-5 and Cr/H-ZSM-5. The purpose of prior dissolution with [BMIM] Cl ionic liquid was to break the structural network of hydrogen bonding in cellulose to achieve easier interaction between catalyst and substrate. Preliminary experimental results were compared to the two catalysts for effective depolymerization of MCC for further investigation. It was found that the H-ZSM-5 catalyst showed better catalytic activity to depolymerize MCC a maximum yield of 70% total reducing sugar while the Cr/H-ZSM-5 catalyst yielded a maximum of 55%. However, Cr/H-ZSM-5 achieved a higher yield of 5-HMF from fructose (53%) while H-ZSM-5 gives a maximum yield of 31% with identical reaction condition. The weak catalytic activity Cr/H-ZSM-5 to depolymerize MCC to total reducing sugar is due to a reduction in Bronsted acid sites due to chromium metal inclusion which generally increases the Lewis acidity at the expense of Bronsted acid sites. For cellulose hydrolysis, higher

247 Bronsted acidity is required to cleave the glycosidic bond while for sugar dehydration, both
248 acidities' optimized acid sites play an essential role.

249 In transforming lignocellulosic biomass to value-added chemicals such as 5-HMF and LA, fructose
250 is considered the ideal substrate with more straightforward conversion and excellent yield of 5-
251 HMF using a wide range of homogeneous as well as heterogeneous catalysts. For instance,
252 chromium chloride ($CrCl_2$, $CrCl_3$) and copper chloride catalysts in an ionic liquid have been
253 reported to be effective for dehydration of sugars to form 5-HMF with a maximum yield of 81%
254 from fructose and 70% using glucose [23][24]. However, the challenge in separation and the high
255 level of chromium toxicity hindered the practical production of 5-HMF. Heterogeneous acid
256 catalysts have easy recovery and production sustainability making them more promising for
257 practical applications in large-scale production than homogenous catalysts [25]. Therefore,
258 catalytic dehydration of fructose to 5-HMF using chromium metal impregnated on H-ZSM-5
259 support (5 % Cr/H-ZSM-5) was tested and the resulted in 87% conversion and 55% yield 5-HMF
260 in [BMIM] Cl-water reaction media. In this study with identical reaction condition, the yield of 5-
261 HMF using Cr/H-ZSM-5 catalyst was found to be effective compared with the yield obtained from
262 H-ZSM-5 catalyst (H-ZSM-5). Therefore, further investigation was carried out to study the effect
263 of temperature and dehydration time on 5-HMF yield.

264 The effect of temperature and reaction time on the dehydration of fructose catalyzed by Cr/H-
265 ZSM-5, using [BMIM] Cl-water as a solvent, has been studied. The yield of 5-HMF showed a
266 pattern of increasing and then decreasing with time at all temperatures studied. At 160 ^{o}C, the yield
267 of 5-HMF increased gradually to 34% up to 60 min, while at 180 ^{o} C it increased rapidly to 53%
268 after 30 min, showing that higher temperature increased the yield of 5-HMF and decreased the
269 dehydration time required. This was further confirmed at 200 ^{o}C with a of yield 47% 5-HMF at 15

min of dehydration time. The maximum yield was achieved at a temperature of 180 ºC and 30 min of reaction time. When the dehydration reaction time was extended over 30 min, the yield of 5-HMF decreased significantly due to decomposition of 5-HMF. The degradation products contain levuilinic acid, formic acid and soluble polymers as observed from HPLC analysis. However, the separated products were exceedingly small to be quantified. In the case of soluble polymers, a wide range of products are possibly available, which is very difficult to obtain the accurate molecular structure and determine the exact product type [25].

The reaction temperature and time have a significant influence on the conversion of glucose to 5-HMF. The conversion of glucose to 5-HMF at a temperature of 200 ° C and 60 min of reaction time yielding a maximum yield of 24% 5-HMF was achieved. The results suggested that as temperature increased, the yield of 5-HMF also increased initially and then followed a decreasing pattern at extended reaction time due to the formation of undesired products such as insoluble humin and soluble polymers [26]. Moreover, the formation of 5-HMF from glucose at 160°C and 180°C at 120 min of reaction time resulted in maximum yield of 17 and 19.5% HMF, respectively. The dehydration of glucose is relatively complex compared with fructose due to the six-membered pyranoside structure. For this reason, the dehydration of glucose to 5-HMF undergoes an additional step of isomerization of glucose to fructose before the dehydration reaction to form 5-HMF using Cr/H-ZSM-5 catalyst.

3.2.3 Mechanism of MCC Hydrolysis

During the hydrolysis of MCC, two steps are essential: the dissolution of MCC in [BMIM] Cl ionic liquid and subsequent hydrolysis in the presence of water as a co-solvent using catalytic amount of H-ZSM-5 catalyst. The purpose of dissolution of MCC alone in the ionic liquid is

primarily to overcome cellulose's recalcitrant behavior and break the hydrogen bonding networking in the cellulose strand. This step is essential to improve the accessibility of β-1, 4-glycosidic linkages between the glucose and create contact between the substrate and catalyst within the reaction media. Besides, prior dissolution helps simplify the structural complexity of cellulose resulting from higher crystallinity and a more significant degree of cellulose polymerization to ease hydrolysis. Mechanistically, the chlorine ions of the ionic liquid are efficient in forming a new hydrogen bonding with the hydroxyl groups of cellulose while the cations prevent the crosslinking of cellulose in the dissolution process. The cations form a linkage with the oxygen of the broken hydroxyl groups of the cellulose and serve as electron acceptors (Figure 6).

The hydrolysis of MCC is described by the Saeman model [27] that the reaction kinetics follows two pseudo-homogeneous consecutive first-order reaction. The degradation products are mainly 5-HMF and humins. The Mechanism of MCC hydrolysis over H-ZSM-5 catalyst is like the hydrolysis of cellulose in the presence of homogeneous acidic catalysts such as sulphuric acids. The glycosidic bonds in cellulose polymer are broken by Bronsted acid sites similar to H^+ ions of acidic solution breaks the bond to release the glucose monomers through binding with the glycosidic oxygen atom leading to hydrolysis of MCC to simple sugars. H+ cations generated in-situ from the Bronsted acid sites of zeolite were the key active species for the effective hydrolysis of cellulose over H-ZSM-5 and the Lewis acid sites do not exhibit high activity as reported from FT-IR through pyridine adsorption [19]. In addition to the catalyst, the H^+ molecules produced from the dissociation of water (co-solvent) participate in the hydrolysis reaction, facilitating the glycosidic bond's cleavage.

3.2.3 Kinetic modeling of MCC depolymerization

Valorization of lignocellulosic biomass requires understanding the mechanism and kinetics of the complex cellulose hydrolysis reaction [28]. The complexity of cellulose hydrolysis emerged from the recalcitrant behavior of cellulose which requires harsh reaction conditions. The hydrolysis products (sugars) have high reactivity that suffers from further decomposition at sever reaction conditions. The incompatibility between the cellulose stability and highly reactive hydrolysis products complicates understanding the reaction mechanism and kinetics of cellulose hydrolysis. However, understanding the mechanism and kinetics of hydrolysis reaction is especially important for process design and optimization. The kinetic modeling for cellulose hydrolysis in the synergetic effect of H-ZSM-5 catalyst and [BMIM] Cl ionic liquid has been studied to investigate the ionic liquid's effect on the rate of reaction, activation energy and mechanism of hydrolysis.

The yield data of TRS were obtained experimentally and data generated from the mathematical model (Eqn 1.4), the activation energy and reaction rate constants (k_1 and k_2) were calculated and compared, and the results are presented in Figure 3. The experiments were performed over a wide temperature range (140 to 200 ºC) and hydrolysis run time (0 to 180 min). The kinetic model used is a model developed by Saeman for cellulose hydrolysis, and the present study assumes irreversible pseudo-homogeneous first-order reactions [27]. The estimate of the kinetic parameters is performed using Polymath 6.0 software. The following assumptions were taken into consideration for model development:

1. The first step in depolymerization of microcrystalline cellulose is the cleavage of β-(1, 4) glycosidic bonds followed by decomposition of TRS to other products 5-HMF and humin.
2. The reaction rate equations were developed based on the Saeman model considering all the model's assumptions [27].

3. The TRS concentration was based on MCC's hydrolysis reaction that includes the major depolymerization products intermediate sugars and oligomers.
4. Mass transfer on the reaction kinetics was insignificant due to the complete dissolution of cellulose in [BMIM] Cl ionic liquid media before depolymerization reaction.
5. It is assumed that dissolved cellulose diffuses into the internal pores of zeolite and the glycosidic bonds of cellulose then extend into the vicinity of Bronsted acid sites where catalytic depolymerization takes place [29].

Hydrolysis of lignocellulosic biomass is an overly complex reaction comprising of formation and decomposition of sugars. Therefore, a simplified kinetic model is used to describe the formation and decomposition of sugar products from cellulose's hydrolysis. The model proposes that cellulose depolymerization involves the hydrolysis of cellulose to reducing sugar and subsequent degradation of sugar to furan chemicals and humin. The reaction scheme for depolymerization of cellulose is shown in Equation 1.1 while the reaction rate constant for thesecond series reaction i.e., TRS decomposition is given in Equation 1.2.

$$\text{Cellulose} \xrightarrow{K_1} \text{TRS (Glucose)} \xrightarrow{K_2} \text{Decomposition products} \qquad (1.1)$$

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C \qquad (1.2)$$

The formation rate of reducing sugars (B) with respect to depolymerization time is represented by Equation 1.4. The integration of Equation 1.4 (considering the following boundary conditions at t =0, $C_{B,0} = 0$) with respect to time gives Equation 1.6 which was used to represent the concentration of total reducing sugar production as a function of time and used to calculate the reaction constants (k_1 (min^{-1}) and k_2 (min^{-1})). The Arrhenius equation describes the correlation of reaction rate constants with the temperature. The activation energies were calculated from the Arrhenius

equations with a reference temperature. For a batch reaction rate of formation of the reactions is given as follow:

$$-r_A = k_1 C_A \quad (1.3)$$

$$r_B = k_1 C_A - k_2 C_B \quad (1.4)$$

$$r_C = k_1 C_A \quad (1.5)$$

The concentration of TRS with time can be calculated as shown in Eqn 1.6 below:

$$C_B = k_1 C_{AO} \left(\frac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1} \right) \quad (1.6)$$

Where C_A is the cellulose concentration (mg ml^{-1}), C_{A0} is the initial concentration of cellulose (mg ml^{-1}), C_B is the total reducing sugars concentration (mg ml^{-1}), C_C is decomposition product concentration and 't' is the depolymerization reaction time (min).

3.2.3 Formation and Degradation of TRS

The application of ionic liquid for catalytic hydrolysis of cellulose to value-added chemicals is a promising approach to overcome the recalcitrant nature of cellulose for a potential scale-up to the bio-refinery scheme. The presence of [BMIM] Cl ionic liquid improved the yield of interest products from microcrystalline cellulose's depolymerization. The role [BMIM] Cl was significant mainly for three reasons: (1) [BMIM] Cl dissolved cellulose entirely within the given substrate loading, (2) the chloride ions in the ionic liquid played the role of base and nucleophile that promoted the isomerization of glucose to fructose and (3) $[BMIM]^+$ of the ionic liquid stabilize dehydration products from further decomposition [30]. Dissolution temperature and time showed

a profound effect on reducing the crystallinity index and degree of cellulose polymerization. Higher the crystallinity and degree of polymerization of cellulose, the less the reactivity to depolymerize to sugar monomers. Therefore, it is imperative to dissolve cellulose and reduce its crystallinity to hydrolyze the substrate effectively. The reduction in crystallinity was achieved through the prior dissolution of cellulose in an ionic liquid followed by the hydrolysis reaction using the catalytic effect of the H-ZSM-5 catalyst.

A kinetic model was constructed based on calculating the best-fit reaction coefficients for k_1 and k_2, as presented in Table 2. The model fitted well with the experimental data for all four temperature sets with an R^2 value greater than 0.96 showing reasonable agreement between the experimental and calculated data. Figure 7 shows the kinetic data and compared with the experimental result. It is observed that the activation energies of formation and decomposition of sugars decreased significantly for [BMIM] Cl ionic liquid media compared with the hydrolysis that takes place in aqueous media [31]. The activation energy of cellulose depolymerization to reducing sugars calculated (E_{a1} = 85.8 kJ mol^{-1}), is less than the calculated activation energy for acid hydrolysis of cellulose in water (Ea_1 = 105 – 188 kJ mol^{-1}) [9]. The activation energy values reported in cellulose hydrolysis using ionic liquid solvent falls in the range of 55 to 89 kJ mol^{-1} which depends on the nature of the ionic liquid and the co-solvent effect [10].

Similarly, the activation energy for decomposition of reducing sugars in ionic liquid was lower (Ea2 = 42.5 kJ mol−1) than aqueous media (E_{a2} = 120 kJ mol^{-1}). The decrease in activation energies for the consecutive reactions can be attributed to the ionic liquid's ionic nature, enhancing the susceptibility of glycosidic bond cleavage to release the sugar monomers. The plot of ln (k) vs. 1/T leads to a straight line with a slope of the fitting line indicating the activation energy and pre-exponential factor is determined by the intercept of the fitting curve as shown in Figure 8 and

reported in the literature [32] for both formation and decomposition of reducing sugar from the depolymerization of cellulose.

4. Conclusion The inert nature of cellulose and insufficient knowledge in solid-solid reaction systems make the heterogeneous catalytic conversion of cellulose ambitious. In our research, porous zeolite materials (H-ZSM-5) and ionic liquid have shown extraordinary ability to perform as catalyst and catalyst support for cellulose conversion. It appears that the mechanism of action of the zeolite catalyst is via the breaking of the glycosidic bonds in cellulose to release the glucose monomers. The closeness of the acidic sites may be essential for cellulose hydrolysis than acidic strength alone.

A kinetic study for MCC hydrolysis using the synergistic effect of [BMIM] Cl ionic liquid was performed over H-ZSM-5. The catalyst was adequate for the MCC's depolymerization up to a yield value of 70% TRS. [BMIM] Cl ionic liquid was highly influential in overcoming cellulosic biomass's recalcitrance by breaking the extensive network of intra and inter-hydrogen bonding and the strong acidity of H-ZSM-5 was able to break the beta-1, 4-glycosidic bond to release sugar molecules. During depolymerization reaction, ionic liquid's presence significantly reduced the activation energy of both the formation and decomposition of sugar obtained from the reaction. The activation energy calculated in cellulose hydrolysis using H-ZSM-5 for a depolymerization time of 180 min was found to be 85.8 kJ mol−1 while the decomposition of reducing sugars in ionic liquid was found to be 42.5 kJ mol−1.**Reference**

[1] R. J. Chimentão, E. Lorente, F. Gispert-Guirado, F. Medina, and F. López, “Hydrolysis of dilute acid-pretreated cellulose under mild hydrothermal conditions,” *Carbohydr. Polym.*, vol. 111, pp. 116–124, 2014, doi: 10.1016/j.carbpol.2014.04.001.

[2] W. Ji, Z. Shen, and Y. Wen, “Hydrolysis of wheat straw by dilute sulfuric acid in a continuous mode,” *Chem. Eng. J.*, vol. 260, pp. 20–27, 2015, doi: 10.1016/j.cej.2014.08.089.

[3] T. Auxenfans, S. Buchoux, K. Djellab, C. Avondo, E. Husson, and C. Sarazin, “Mild pretreatment and enzymatic saccharification of cellulose with recycled ionic liquids towards one-batch process,” *Carbohydr. Polym.*, vol. 90, no. 2, pp. 805–813, 2012, doi: 10.1016/j.carbpol.2012.05.101.

[4] Y. Chen, G. Li, F. Yang, and S. Zhang, “Mn / ZSM-5 participation in the degradation of cellulose under phosphoric acid media,” *Polym. Degrad. Stab.*, vol. 96, no. 5, pp. 863–869, 2011, doi: 10.1016/j.polymdegradstab.2011.02.007.

[5] C. Abels, K. Thimm, H. Wulfhorst, A. Christine, and M. Wessling, “Bioresource Technology Membrane-based recovery of glucose from enzymatic hydrolysis of ionic liquid pretreated cellulose,” *Bioresour. Technol.*, vol. 149, pp. 58–64, 2013, doi: 10.1016/j.biortech.2013.09.012.

[6] J. Wang, J. Xi, and Y. Wang, “Recent advances in the catalytic production of glucose from lignocellulosic biomass,” *Green Chem.*, vol. 17, no. 2, pp. 737–751, 2015, doi: 10.1039/C4GC02034K.

[7] J. Verendel, T. Church, and P. Andersson, “Catalytic One-Pot Production of Small Organics from Polysaccharides,” *Synthesis (Stuttg).*, vol. 2011, no. 11, pp. 1649–1677, Apr. 2011, doi: 10.1055/s-0030-1260008.

[8] H. T. Vo, V. T. Widyaya, J. Jae, H. S. Kim, and H. Lee, “Hydrolysis of ionic cellulose to glucose,” *Bioresour. Technol.*, vol. 167, pp. 484–489, 2014, doi:

10.1016/j.biortech.2014.06.025.

[9] Y.-B. Huang and Y. Fu, “Hydrolysis of cellulose to glucose by solid acid catalysts,” *Green Chem.*, vol. 15, no. 5, p. 1095, 2013, doi: 10.1039/c3gc40136g.

[10] A. Brandt, J. Gräsvik, J. P. Hallett, and T. Welton, “Deconstruction of lignocellulosic biomass with ionic liquids,” *Green Chem.*, vol. 15, no. 3, pp. 550–583, 2013, doi: 10.1039/c2gc36364j.

[11] Y. Fukaya, K. Hayashi, and H. Ohno, “Cellulose dissolution with polar ionic liquids under mild conditions : required factors for anions {,” no. Chart 1, pp. 44–46, 2008, doi: 10.1039/b713289a.

[12] X. Tong, Y. Ma, and Y. Li, “Applied Catalysis A : General Biomass into chemicals : Conversion of sugars to furan derivatives by catalytic processes,” *"Applied Catal. A, Gen.*, vol. 385, no. 1–2, pp. 1–13, 2010, doi: 10.1016/j.apcata.2010.06.049.

[13] S. Kassaye, C. Pagar, K. K. Pant, S. Jain, and R. Gupta, “Bioresource Technology Depolymerization of microcrystalline cellulose to value added chemicals using sulfate ion promoted zirconia catalyst,” *Bioresour. Technol.*, vol. 220, pp. 394–400, 2016, doi: 10.1016/j.biortech.2016.08.109.

[14] X. Cao *et al.*, “Impact of regeneration process on the crystalline structure and enzymatic hydrolysis of cellulose obtained from ionic liquid.,” *Carbohydr. Polym.*, vol. 111, pp. 400–3, Oct. 2014, doi: 10.1016/j.carbpol.2014.05.004.

[15] P. K. Rout, A. D. Nannaware, O. Prakash, A. Kalra, and R. Rajasekharan, “Synthesis of hydroxymethylfurfural from cellulose using green processes: A promising biochemical and

biofuel feedstock," *Chem. Eng. Sci.*, vol. 142, pp. 318–346, 2016, doi: 10.1016/j.ces.2015.12.002.

[16] S. Kassaye, K. K. Pant, and S. Jain, "Synergistic effect of ionic liquid and dilute sulphuric acid in the hydrolysis of microcrystalline cellulose," *Fuel Process. Technol.*, vol. 148, pp. 289–294, 2016, doi: 10.1016/j.fuproc.2015.12.032.

[17] H. E. van der Bij and B. M. Weckhuysen, "Local silico-aluminophosphate interfaces within phosphated H-ZSM-5 zeolites.," *Phys. Chem. Chem. Phys.*, vol. 16, no. 21, pp. 29–32, 2014, doi: 10.1039/c3cp54791d.

[18] N. Mimura, M. Okamoto, H. Yamashita, S. T. Oyama, and K. Murata, "Oxidative dehydrogenation of ethane over Cr/ZSM-5 catalysts using CO2 as an oxidant.," *J. Phys. Chem. B*, vol. 110, no. 43, pp. 21764–70, 2006, doi: 10.1021/jp061966l.

[19] H. Cai, C. Li, A. Wang, G. Xu, and T. Zhang, "Applied Catalysis B : Environmental Zeolite-promoted hydrolysis of cellulose in ionic liquid , insight into the mutual behavior of zeolite , cellulose and ionic liquid," *"Applied Catal. B, Environ.*, vol. 123–124, pp. 333–338, 2012, doi: 10.1016/j.apcatb.2012.04.041.

[20] H. Liu, H. Wei, W. Xin, and C. Song, "Differences between Zn / HZSM-5 and Zn / HZSM-11 zeolite catalysts in alkylation of benzene with dimethyl ether," *J. Energy Chem.*, vol. 23, no. 5, pp. 617–624, 2014, doi: 10.1016/S2095-4956(14)60192-3.

[21] A. M. Santa Arango, C. M. Escobar Garcés, J. L. Agudelo Valderrama, A. Guzmán Monsalve, L. A. Palacio Santos, and A. Echavarría Isaza, "Oligomerization of propene over ZSM-5 modified with Cr and W," *Rev. Fac. Ing.*, no. 57, pp. 57–65, 2011.

[22] I. G. Baek, S. J. You, and E. D. Park, “Bioresource Technology Direct conversion of cellulose into polyols over Ni / W / SiO 2 -Al 2 O 3,” *Bioresour. Technol.*, vol. 114, pp. 684–690, 2012, doi: 10.1016/j.biortech.2012.03.059.

[23] S. Bali, M. A. Tofanelli, R. D. Ernst, and E. M. Eyring, “Chromium (III) catalysts in ionic liquids for the conversion of glucose to 5- (hydroxymethyl) furfural (HMF): Insight into metal catalyst : ionic liquid mediated conversion of cellulosic biomass to biofuels and chemicals,” *Biomass and Bioenergy*, vol. 42, no. Iii, pp. 224–227, 2012, doi: 10.1016/j.biombioe.2012.03.016.

[24] H. Zhao, J. E. Holladay, H. Brown, and Z. C. Zhang, “Reports 8.,” vol. 113409, no. 2005, 2006.

[25] H. Xu *et al.*, “Dehydration of fructose into 5-hydroxymethylfurfural by high stable ordered mesoporous zirconium phosphate,” *Fuel*, vol. 145, pp. 234–240, 2015, doi: 10.1016/j.fuel.2014.12.072.

[26] L. Hu, Z. Wu, J. Xu, Y. Sun, L. Lin, and S. Liu, “Zeolite-promoted transformation of glucose into 5-hydroxymethylfurfural in ionic liquid,” *Chem. Eng. J.*, vol. 244, pp. 137–144, 2014, doi: 10.1016/j.cej.2014.01.057.

[27] J. F. Saeman, “Hydrolysis of Cellulose and Decomposition of Sugars in Dilute Acid at High Temperature,” *Ind. Eng. Chem.*, vol. 37, no. 9, pp. 43–52, 1945, doi: Doi 10.1021/Ie50421a009.

[28] L. Negahdar, I. Delidovich, and R. Palkovits, “Aqueous-phase hydrolysis of cellulose and hemicelluloses over molecular acidic catalysts: Insights into the kinetics and reaction mechanism,” *Appl. Catal. B Environ.*, vol. 184, pp. 285–298, 2016, doi:

509 10.1016/j.apcatb.2015.11.039.

510 [29] F. Guo, Z. Fang, C. C. Xu, and R. L. Smith, “Solid acid mediated hydrolysis of biomass for
511 producing biofuels,” *Prog. Energy Combust. Sci.*, vol. 38, no. 5, pp. 672–690, 2012, doi:
512 10.1016/j.pecs.2012.04.001.

513 [30] L. Hu *et al.*, “Catalytic conversion of carbohydrates into 5-hydroxymethylfurfural over
514 cellulose-derived carbonaceous catalyst in ionic liquid.,” *Bioresour. Technol.*, vol. 148, pp.
515 501–7, Nov. 2013, doi: 10.1016/j.biortech.2013.09.016.

516 [31] A. J. Kunov-Kruse, A. Riisager, S. Saravanamurugan, R. W. Berg, S. B. Kristensen, and R.
517 Fehrmann, “Revisiting the Bronsted acid catalysed hydrolysis kinetics of polymeric
518 carbohydrates in ionic liquids by in situ ATR-FTIR spectroscopy,” *Green Chem.*, vol. 15,
519 no. 10, pp. 2843–2848, 2013, doi: 10.1039/c3gc41174e.

520 [32] M. Mohan, T. Banerjee, and V. V Goud, “Hydrolysis of bamboo biomass by subcritical
521 water treatment.,” *Bioresour. Technol.*, vol. 191, pp. 244–252, 2015, doi:
522 10.1016/j.biortech.2015.05.010.

523

Table 1. BET surface area analysis of H-ZSM-5 and Cr/H-ZSM-5 catalysts

Catalyst Type	**BET surface area (m^2/g)**
H-ZSM-5	270.0
Cr/H-ZSM-5	248.2

Table 2. Kinetic rate constants at different temperatures

Temperature (°C)	k_1 (min^{-1})	k_2 (min^{-1})
140	0.0010	0.0006
160	0.0042	0.0019
180	0.0094	0.0020
200	0.0244	0.0035

Figures

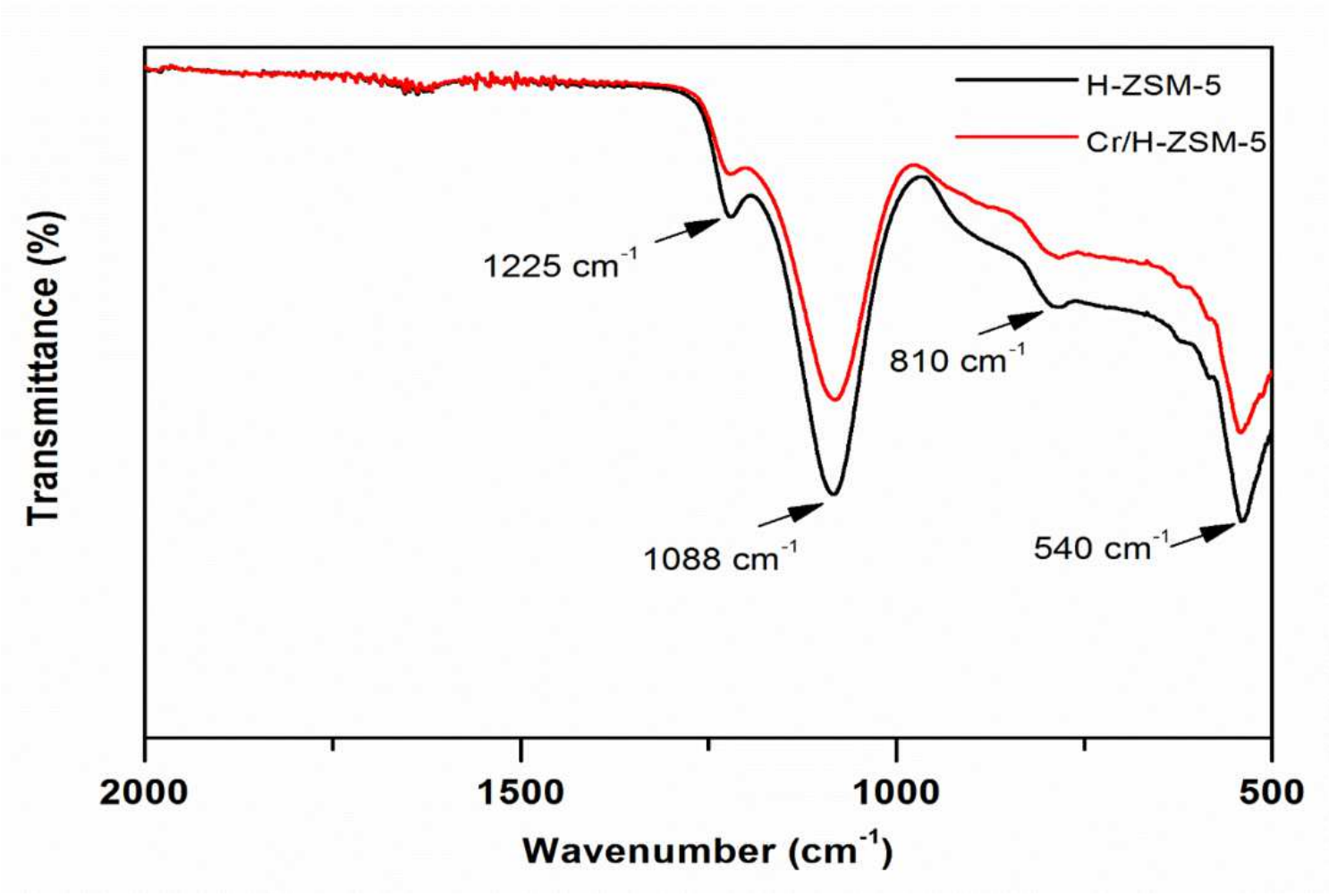


Figure 1

FTIR analysis of H-ZSM-5 and Cr/H-ZSM-5 catalysts

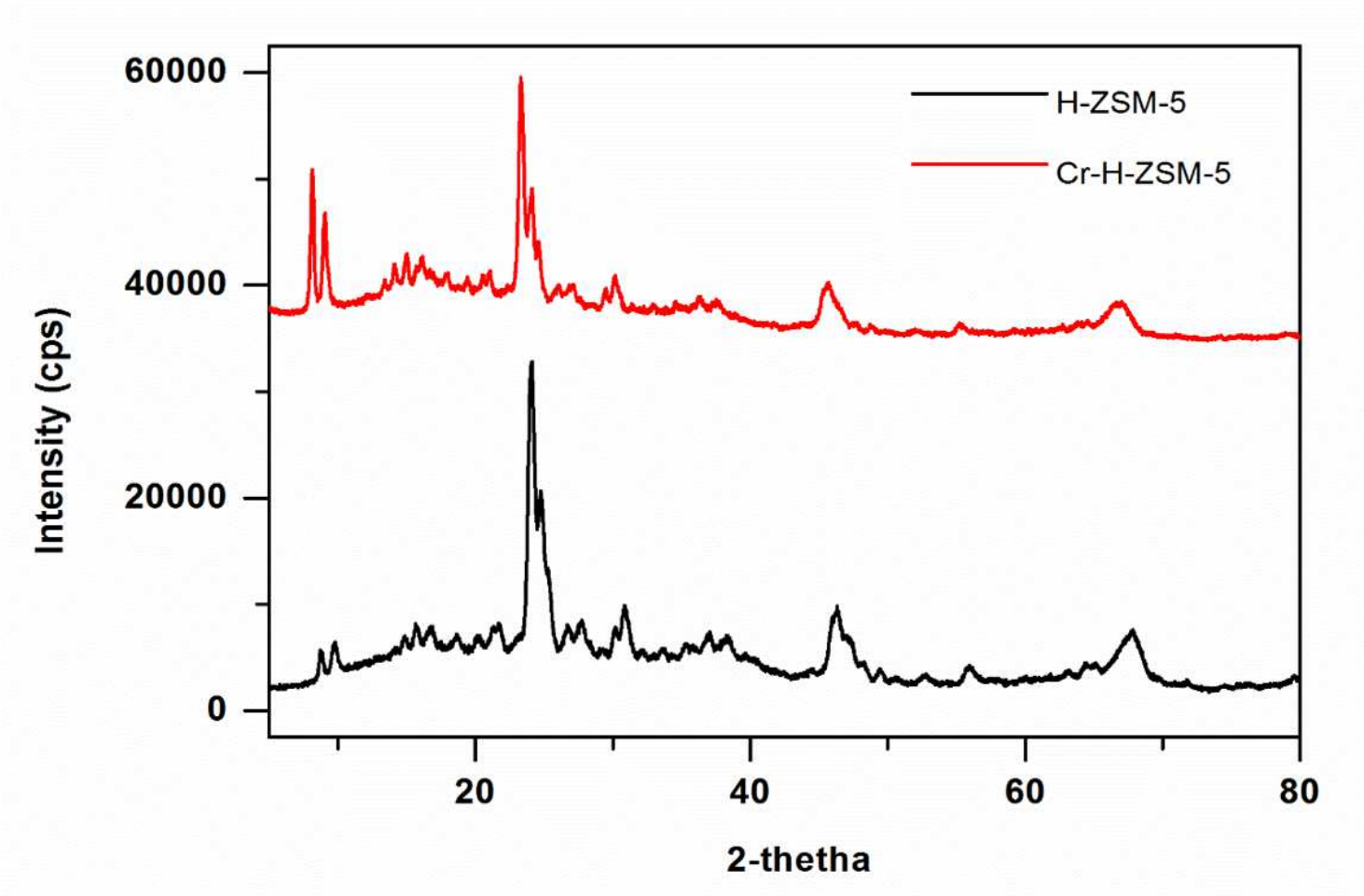


Figure 2

XRD pattern of H-ZSM-5 and Cr/H-ZSM-5 catalysts

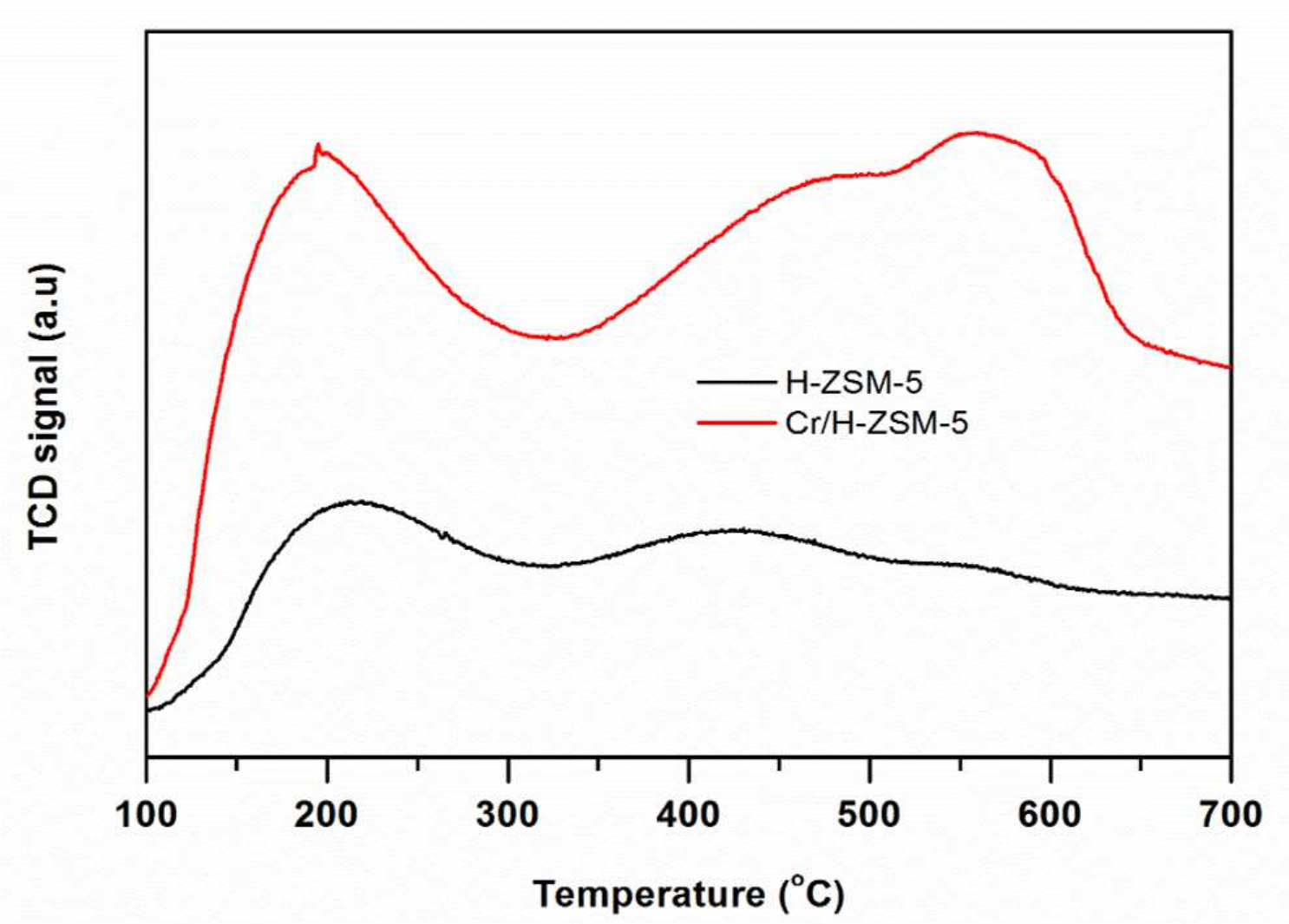


Figure 3

Ammonia-TPD analysis of H-ZSM-5 and Cr/H-ZSM-5 catalysts

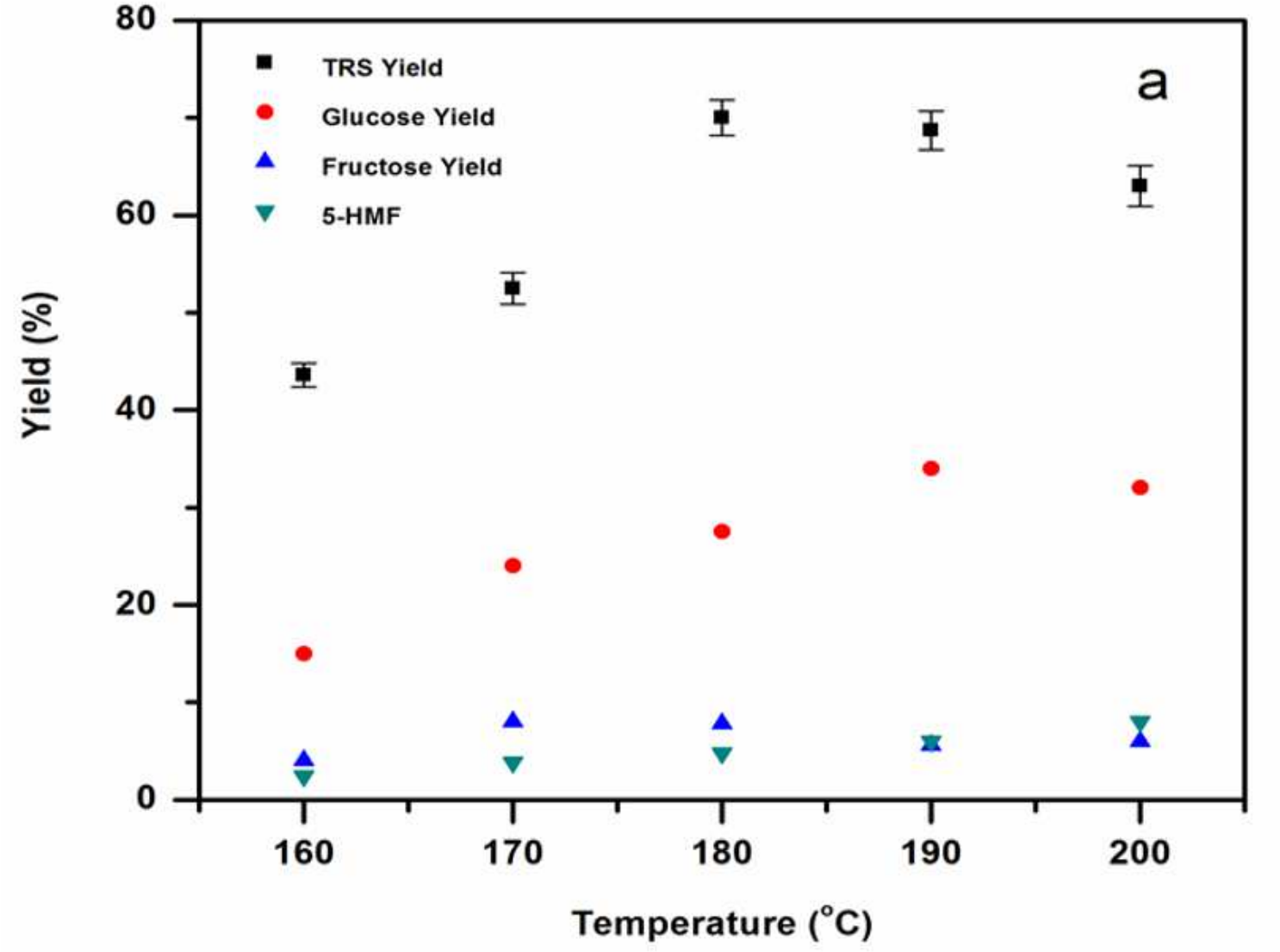


Figure 4

Effect of hydrolysis temperature on TRS yield (catalyst to substrate ratio of 2:1 (w/w) and 180 min of reaction time)

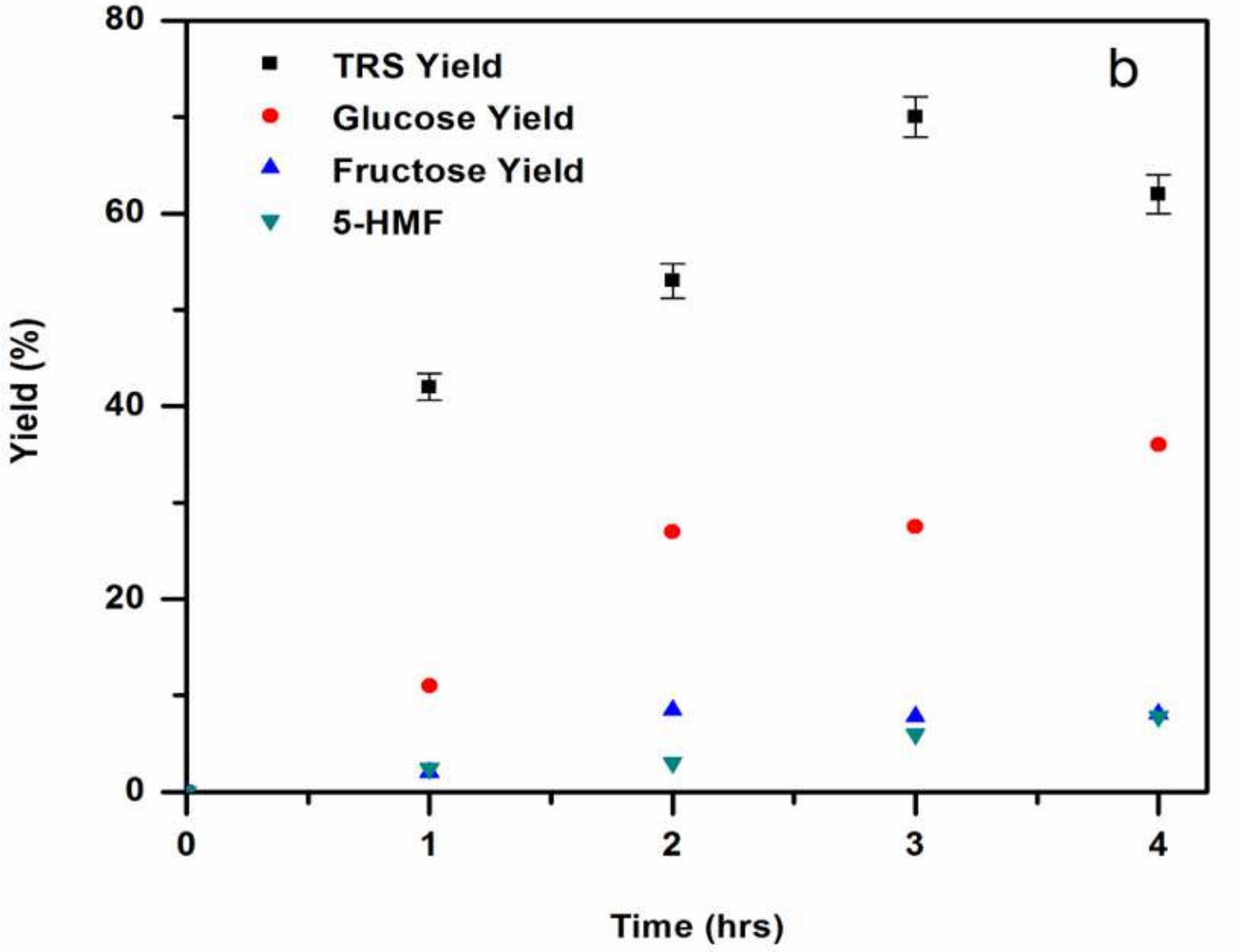


Figure 5

Effect of hydrolysis time on yield of TRS (temperature 180 oC, catalyst to substrate ratio of 2:1 (w/w))

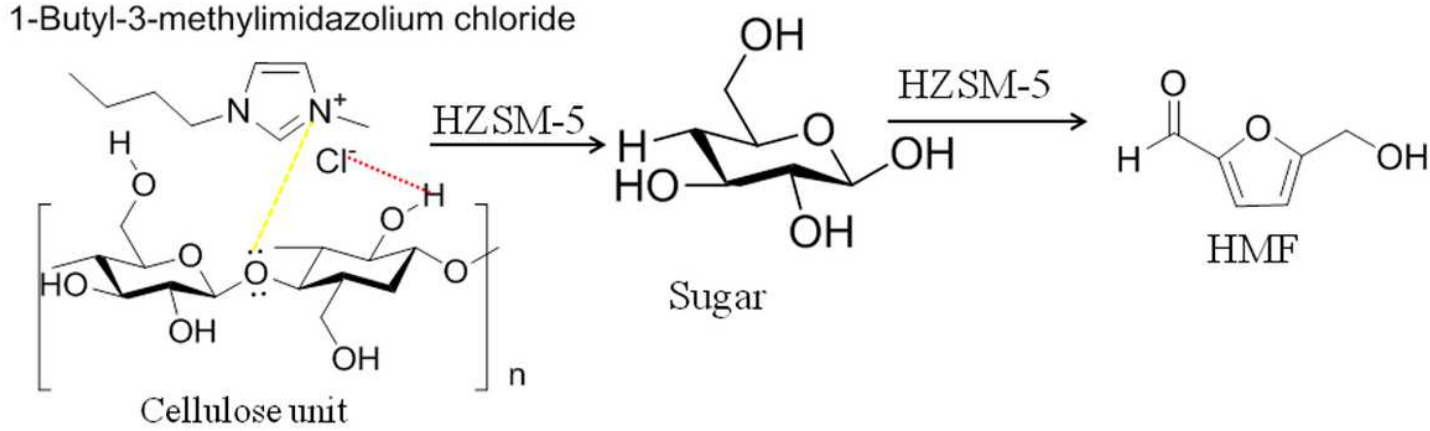


Figure 6

Mechanism of Cellulose Hydrolysis over H-ZSM-5 catalyst in the presence of [BMIM] Cl ionic liquid

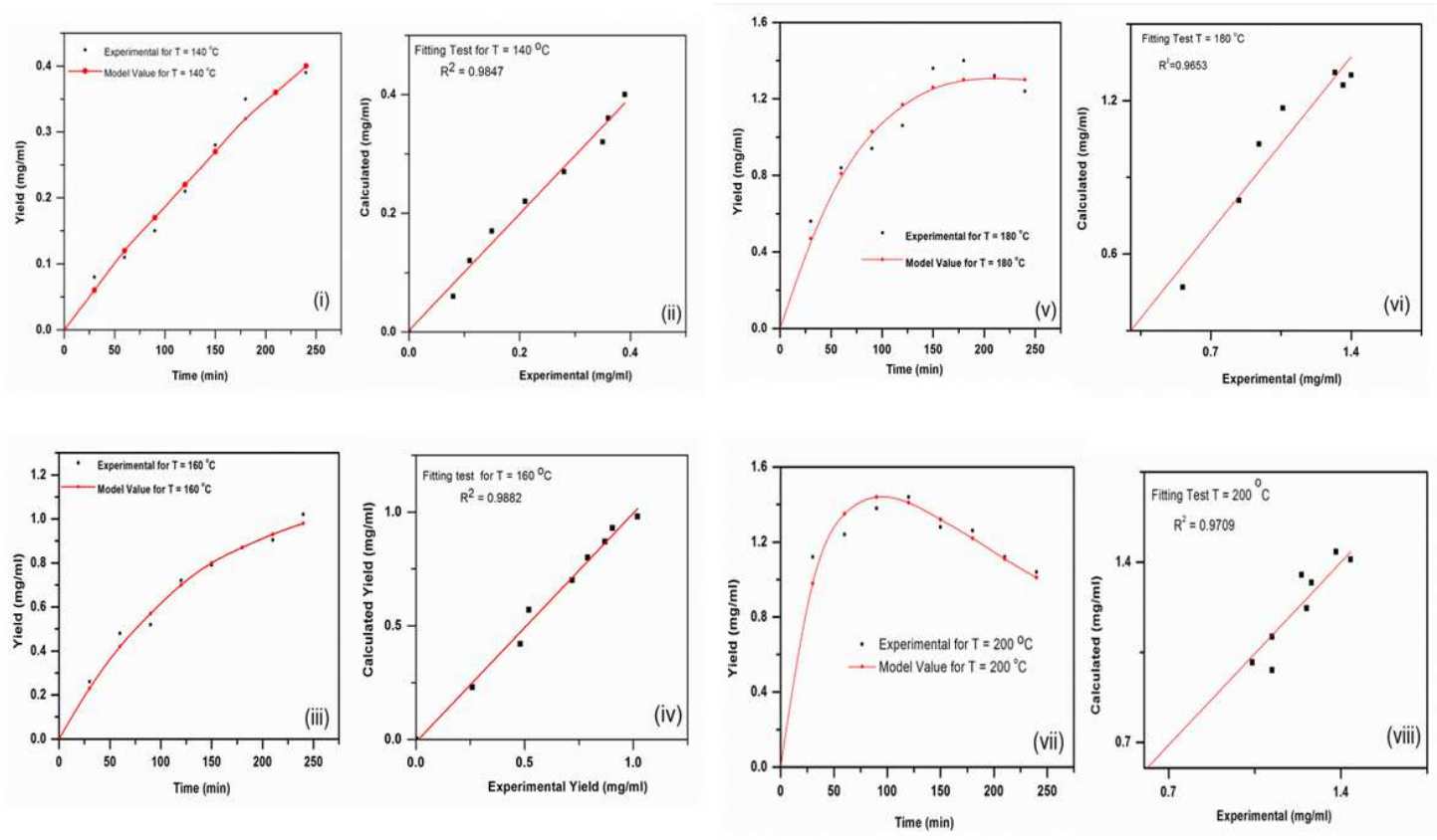
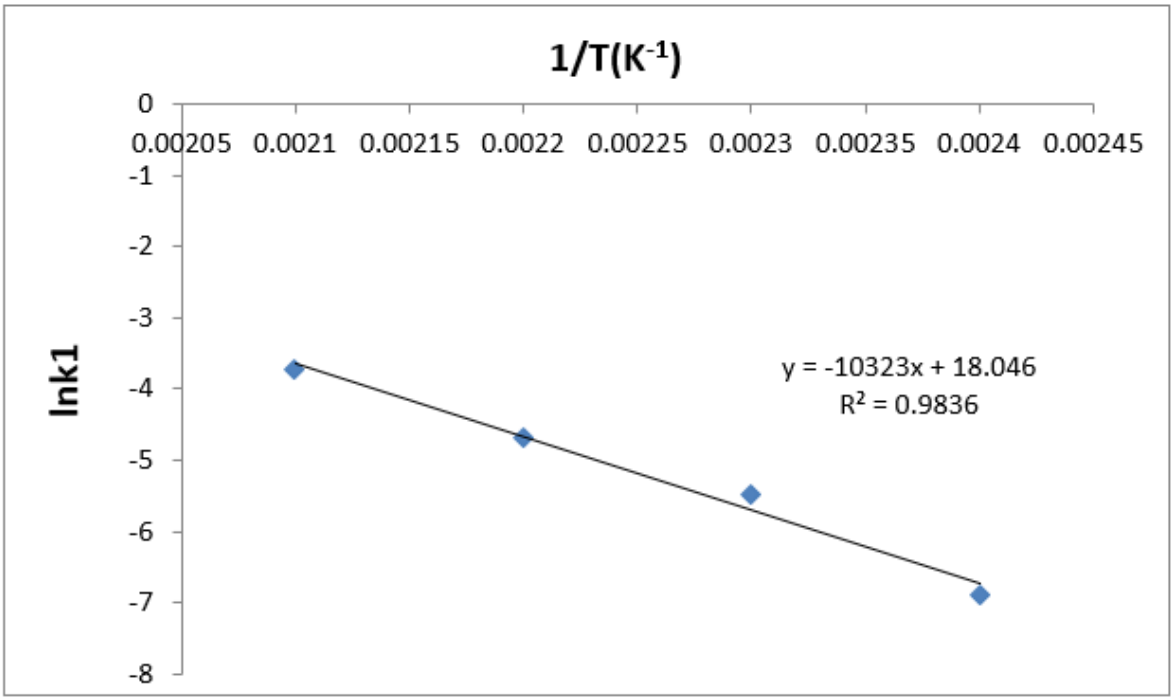


Figure 7

Kinetic modelling of cellulose hydrolysis using H-ZSM-5 catalyst in [BMIM] Cl-water media



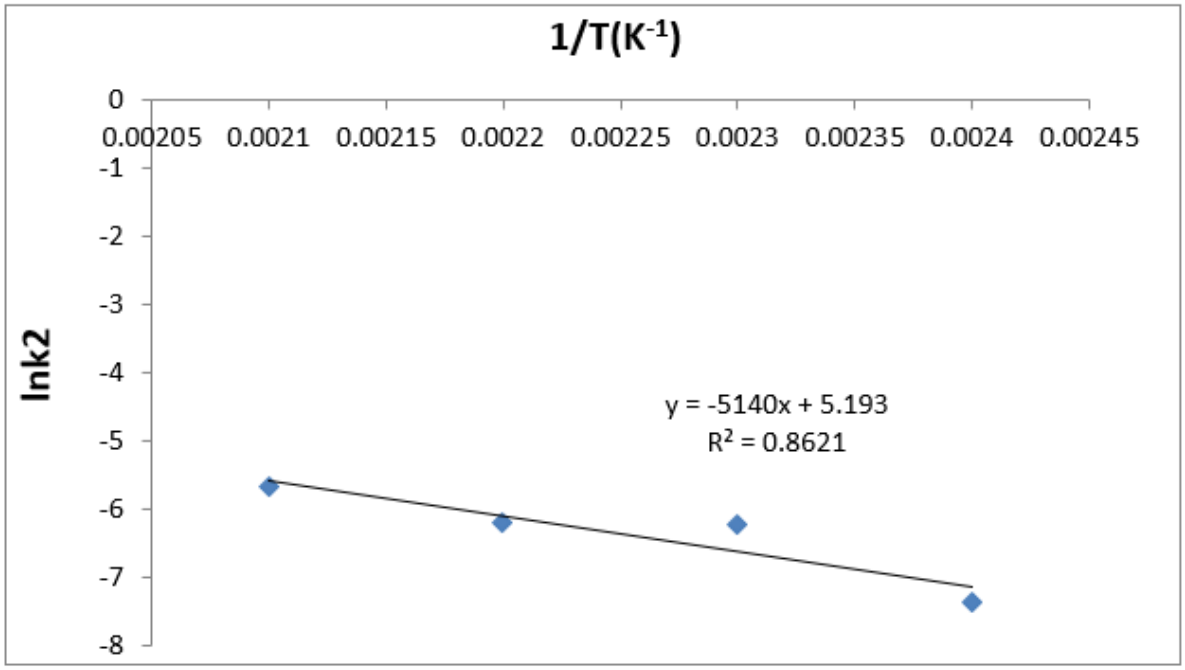


Figure 8

Determination of rate constants for cellulose hydrolysis using H-ZSM-5 catalyst in [BMIM] Cl