

Efficient hydrolysis of cellulose over a magnetic lignin-derived solid acid catalyst in 1-butyl-3-methylimidazolium chloride

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Abstract—A green and efficient strategy for the hydrolysis of cellulose was developed by using a magnetic lignin-derived solid acid catalyst (MLC-SO₃H) in the presence of ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl). The results indicated that reaction temperature, reaction time, catalyst loading and water content have a big influence on the yield of total reducing sugars (TRS). By optimizing these reaction parameters, 69.3% TRS yield was observed at 140 °C for 150 min with the addition of 40 wt% MLC-SO₃H and 1 wt% water. More importantly, MLC-SO₃H could be easily separated from the reaction mixture with an external magnet and could be repeatedly used five times without an obvious loss of catalytic activity, demonstrating that it possessed excellent recyclability. Furthermore, a plausible mechanism involving three consecutive processes of dissolution, adsorption and catalysis for the hydrolysis of cellulose in [BMIM]Cl over a catalyst of MLC-SO₃H was also proposed.

Keywords: Cellulose, Hydrolysis, Total Reducing Sugars, Ionic Liquid, Magnetic Lignin-derived Solid Acid Catalyst

INTRODUCTION

The continuous depletion of worldwide fossil resources and the progressive increase in global energy demands has generated considerable interest in lignocellulosic biomass, which is renewable, widespread, abundant, diverse and inexpensive [1-3]. As the most abundant component of lignocellulosic biomass, cellulose, which is a linear polymer formed by the repeating connection of glucose units via β -1,4-glycosidic bonds, is considered to be an inexhaustible raw material for the sustainable production of chemicals and fuels [4-7]. However, the hydrolysis of cellulose into glucose or other reducing sugars is the primary and essential step for the effective utilization of cellulose [8-11].

Due to the presence of a large number of hydroxyl (-OH) groups, there are numerous intramolecular and intermolecular hydrogen bonds in cellulose [12-14], leading to an intricate supramolecular structure and strong mechanical strength. As a consequence, cellulose is insoluble in water and most common organic solvents [15-18], which results in a serious problem in the hydrolysis of cellulose. Gratifyingly, in recent years, ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) with a sequence of special physicochemical properties such as negligible vapor pressure, high thermal stability, broad electrochemical window, low flammability, high conductivity and close to infinite structural variation [19-23] has been proven to have a remarkable ability to dissolve cellulose through hydrogen-bonding interactions between -OH groups of cellulose

and chlorine anions of [BMIM]Cl [24-28]. Hence, compared to water and most common organic solvents, [BMIM]Cl is a good solvent for the hydrolysis of cellulose.

In addition to an appropriate solvent, the exploitation of a green and efficient acid catalyst is another key point for the hydrolysis of cellulose. Over a long period of time, mineral acids and cellulases are the most common catalysts for the hydrolysis of cellulose. Although they show superior activities, their practical applications are difficult due to a range of serious problems, such as reactor corrosion, waste treatment and poor recyclability and high cost, low efficiency and long reaction time [29-31], respectively. To overcome these drawbacks, many types of solid acid catalysts such as ion-exchange resins [32], metal oxides [33], H-form zeolites [34], hybrid heteropolyacids [35], functionalized silicas [36] and supported metals [37] have been prepared and applied to the hydrolysis of cellulose. Compared to these conventional solid acid catalysts, the more cheaper carbon-based solid acid catalysts, which are generally prepared by the incomplete carbonization of carbohydrates and the subsequent sulfonation of the resulting amorphous carbons, have been regarded as a novel type of solid acid catalysts and also widely used for the hydrolysis of cellulose in recent years [38-40]. However, carbon-based solid acid catalysts possess a common disadvantage related to the lower specific surface areas, which can limit their catalytic activity. Moreover, although carbon-based solid acid catalysts are separable in theory, they are not easy to separate with the hydrolysis residues of cellulose, which can affect their recyclability. Therefore, the development of an easy-to-separate carbon-based solid acid catalyst with a high specific surface area is necessary and important for the hydrolysis of cellulose.

In our previous work [41], we prepared a magnetic lignin-derived

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solid acid catalyst (MLC-SO₃H) by using the enzymatic hydrolysis lignin residue (EHL) as a precursor via a simple impregnation-carbonization-sulfonation process. Surprisingly, MLC-SO₃H possessed a porous structure with a high surface area of 234.61 m²·g⁻¹, it not only exhibited outstanding catalytic performance for the dehydration of glucose and fructose into 5-hydroxymethylfurfural (HMF), but also demonstrated excellent magnetic separation property and reusability. On the basis of the above results, we speculate that MLC-SO₃H should be a proper catalyst for the hydrolysis of cellulose. To gain an insight into this speculation, we used MLC-SO₃H to evaluate its catalytic activity for the hydrolysis of cellulose in the presence of [BMIM]Cl. To achieve a higher yield of total reducing sugars (TRS), various reaction parameters such as reaction temperature, reaction time, catalyst loading and water content were optimized in detail. Furthermore, the recyclability of catalyst and the plausible mechanism for the hydrolysis of cellulose were also investigated.

MATERIALS AND METHODS

1. Materials

1-Butyl-3-methylimidazolium chloride ([BMIM]Cl, 99%) was supplied by Shanghai ChengJie Chemical Co. Ltd. (Shanghai, China). Microcrystalline cellulose, glucose, concentrated sulfuric acid (H₂SO₄, 98%) and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification. Magnetic lignin-derived amorphous carbon (MLC) and MLC-SO₃H were synthesized and characterized according to our previous work [41].

2. Catalyst Preparation

10 g EHL was added into 1,000 mL FeCl₃ solution with a concentration of 10 mmol·L⁻¹, and the mixture was stirred at 300 rpm for 5 h. Then, the water in the mixture was evaporated, and the remaining mixture was dried in a vacuum oven at 65 °C for 12 h. After grinding to 120 mesh, the impregnated EHL with an Fe content of approximately 1 mmol·g⁻¹ was obtained. Subsequently, the Fe-impregnated EHL was carbonized at 400 °C for 1 h under nitrogen atmosphere to produce the magnetic lignin-derived amorphous carbon (MLC). The resulting MLC was then mixed with concentrated H₂SO₄ (the ratio of solid and liquid=1 : 10), and the mixture was heated at 150 °C for 10 h under nitrogen atmosphere to introduce -SO₃H groups. Soon afterwards, the mixture was cooled to room temperature and diluted with 1,000 mL deionized water, which was followed by filtrating and washing with hot deionized water (>80 °C) until the sulfate ions were no longer detected in the washed water. Finally, the resulting catalyst (MLC-SO₃H) was dried in a vacuum oven at 65 °C for 12 h. For comparison, another carbon-based catalyst (LC-SO₃H) was also synthesized by the same procedure using EHL without Fe-impregnating as a precursor.

3. Typical Procedure for the Hydrolysis of Cellulose

In a typical reaction, 50 mg cellulose was first added into 1 g [BMIM]Cl and heated with vigorous stirring at 100 °C in an oil-bath to form a transparent solution. Subsequently, 30 mg catalyst and 0.01 g deionized water were added and heated at 120 °C for 2 h in a closed reactor. At the end of the reaction, the reaction mixture was immediately quenched in an ice-water bath and diluted with 10 mL deionized water. After centrifuging at 10,000 rpm for 5 min,

the supernatant was subjected to the analysis of TRS.

4. TRS Analysis

TRS was measured by using the method of 3,5-dinitrosalicylic acid (DNS) according to the reported procedure [42-44]. More specifically, 1 mL diluted supernatant was transferred to a graduated test tube with stopper and 2 mL DNS reagent was added and the mixed solution was heated at 100 °C for 5 min. Soon afterwards, the above heated solution was quickly cooled down to room temperature in an ice-water bath and 12 mL deionized water was added. The absorbance of the resulting solution was measured at 540 nm on a 721 spectrophotometer (Shanghai, China), and the concentration of TRS was calculated by employing a standard curve obtained with glucose. The mass and yield of TRS were calculated as follows:

$$\text{TRS mas (mg)}=C\times V\times N \quad (1)$$

$$\text{TRS yield (\%)}=\text{TRS mass}/M\times 0.9\times 100 \quad (2)$$

where C is the concentration of TRS, V is the volume of supernatant, N is the dilution multiple of supernatant and M is the initial mass of cellulose.

RESULTS AND DISCUSSION

1. Preliminary Study on the Hydrolysis of Cellulose

The catalytic activity of MLC-SO₃H as well as MLC, LC-SO₃H and H₂SO₄ was initially studied for the hydrolysis of cellulose in the presence of [BMIM]Cl; the results are shown in Fig. 1. In the absence of any other catalyst, only 0.9% TRS yield was obtained, distinctly indicating that [BMIM]Cl had no obvious catalytic activity and it acted merely as a solvent in the hydrolysis of cellulose. When MLC-SO₃H was used as a catalyst under the same reaction conditions, the yield of TRS was sharply improved to 29.4%, which was higher than 22.9% achieved by H₂SO₄. As mentioned in our

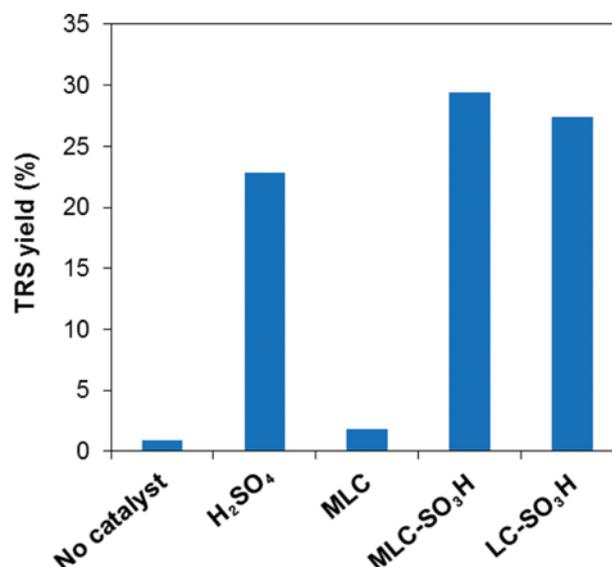


Fig. 1. Hydrolysis of cellulose using various acid catalysts. Reaction conditions: 50 mg cellulose, 30 mg acid catalyst, 0.01 g water, 1 g [BMIM]Cl, 120 °C, 120 min. Note: the amount of H₂SO₄ is 0.0116 mmol that is corresponding to 30 mg MLC-SO₃H.

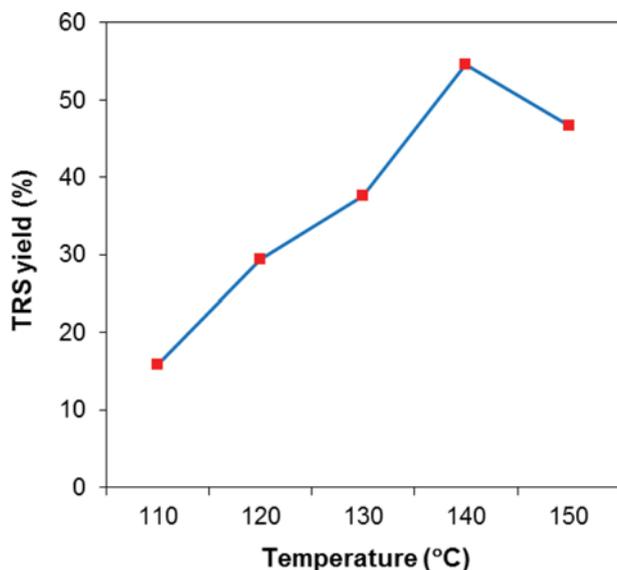


Fig. 2. Effect of reaction temperature on the hydrolysis of cellulose. Reaction conditions: 50 mg cellulose, 30 mg MLC-SO₃H, 0.01 g water, 1 g [BMIM]Cl, 120 min.

previous work, in addition to -SO₃H groups, MLC-SO₃H also possessed -COOH and phenolic -OH groups [41], which is different from H₂SO₄ with single functional groups. Namely, the presence of -COOH and phenolic -OH groups was vital for the hydrolysis of cellulose, because they were proved to have a strong affinity to cellulose through the formation of hydrogen bonds with -OH groups of cellulose [45-47]. However, when MLC without -SO₃H groups was used as a catalyst, only 1.8% TRS yield was observed, obviously demonstrating that -SO₃H groups played a key role for the hydrolysis of cellulose. As a consequence, the synergic effect of -COOH, phenolic -OH and -SO₃H groups should be the reason for the excellent catalytic activity of MLC-SO₃H. It is also noteworthy that in comparison to LC-SO₃H, the introduction of magnetic property in MLC-SO₃H could promote the hydrolysis of cellulose to a certain extent, which is due to the higher acid density, total acid density and BET surface area of MLC-SO₃H caused by Fe₃O₄ [41].

2. Effect of Reaction Temperature

As can be seen from Fig. 2, when the reaction temperature was 110 °C, the yield of TRS was only 15.8%. When the reaction temperature was increased from 120 to 140 °C, TRS yield was correspondingly increased from 29.4 to 54.6%. Generally, in a certain range, the higher the reaction temperature, the higher the yield of TRS. The following two reasons should be responsible for this phenomenon. With the increase of reaction temperature, on the one hand, the physical barrier of activation energy in the hydrolysis of cellulose could be overcome. On the other hand, the viscosity of [BMIM]Cl was gradually decreased and this would be beneficial for the mass transfer between catalyst and cellulose [48]. However, when the reaction temperature was further increased to 150 °C, TRS yield was sharply decreased to 46.7%, which may be attributed to the fact that too much higher temperature resulted in the occurrence of side reactions. As reported, the decomposition of the formed reducing sugars such as glucose into HMF was one of the main side reactions in the hydrolysis of cellulose [39]. In the pres-

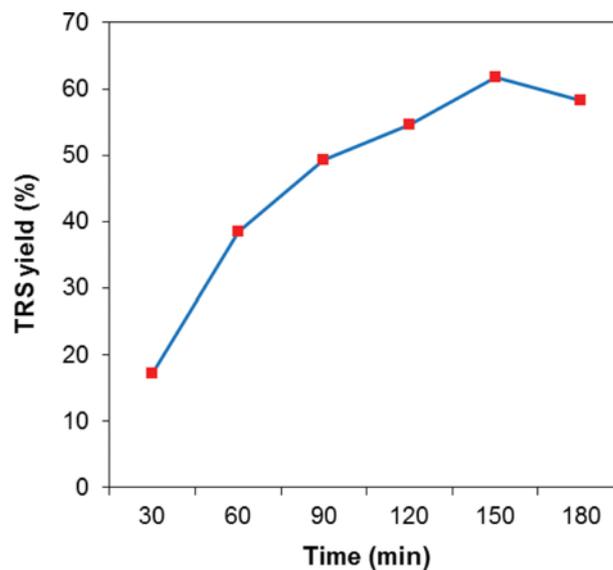


Fig. 3. Effect of reaction time on the hydrolysis of cellulose. Reaction conditions: 50 mg cellulose, 30 mg MLC-SO₃H, 0.01 g water, 1 g [BMIM]Cl, 140 °C.

ent work, the yield of HMF at 150 °C was detected to be 5.9% by means of HPLC. Hence, there is no doubt that the reaction temperature has a large effect on the hydrolysis of cellulose and the stability of hydrolysate. On the basis of the above results, the appropriate reaction temperature was set to 140 °C.

3. Effect of Reaction Time

As presented in Fig. 3, only 17.2% TRS yield was obtained in 30 min at 140 °C. When the reaction time was prolonged to 150 min, the yield of TRS prominently increased to 61.8%. However, when the reaction time was further prolonged to 180 min, TRS yield was decreased to 58.2%. It is well known that the yield of TRS is limited by the equilibrium between cellulose hydrolysis and glucose decomposition [39]. At the beginning of the reaction, the hydrolysis rate of cellulose was probably greater than the decomposition rate of glucose; thus, TRS yield slowly increased with the prolonging of reaction time. When the hydrolysis rate of cellulose was equal to the decomposition rate of glucose, the yield of TRS came to a maximum. After that, the decomposition rate of glucose was greater than the hydrolysis rate of cellulose, TRS yield began to decrease, which is consistent with the trend of the results in Fig. 3. Based on this, the reaction time of 150 min was suitable at the

Table 1. Effect of catalyst loading on the hydrolysis of cellulose^a

Entry	Catalyst loading (wt%)	TRS yield (%)
1	10	33.4
2	20	50.0
3	40	69.3
4	60	61.8
5	80	55.5
6	100	52.9

^aReaction conditions: 50 mg cellulose, 0.01 g water, 1 g [BMIM]Cl, 140 °C, 150 min

Note: The loading of catalyst is relative to the mass of cellulose

Table 2. Comparison of various solid acid catalysts for the hydrolysis of cellulose^a

Entry	Cellulose concentration (wt%)	Catalyst, loading (wt%)	Temperature (°C), time (min)	TRS yield (%)	Reference
1	5.0	MLC-SO ₃ H, 40	140, 150	69.3	This work
2	5.0	Amberlyst-15, 20	100, 300	25.0	[32]
3 ^b	1.0	Nafion-NR50, 50	160, 240	16.0	[50]
4 ^b	6.7	SBA-15-SO ₃ H, 150	150, 180	52.0	[52]
5 ^b	2.0	Cs ₁ H ₂ PW ₁₂ O ₄₀ , 60	160, 360	30.1	[51]
6	5.0	H β , 200	130, 120	55.0	[34]
7	5.0	PCM-SO ₃ H, 100	130, 180	68.9	[49]
8	8.0	Fe ₃ O ₄ @SiO ₂ -SO ₃ H, 63	130, 480	73.2	[48]

^aThe solvent is [BMIM]Cl. Note: the concentration of cellulose is relative to the mass of [BMIM]Cl and the loading of catalyst is relative to the mass of cellulose

^bThe solvent is water

reaction temperature of 140 °C.

4. Effect of Catalyst Loading

As listed in Table 1, when the loading of MLC-SO₃H was 10 wt%, the yield of TRS was only 33.4%. With the increase of MLC-SO₃H loading from 20 to 40 wt%, TRS yield remarkably increased from 50.0 to 69.3%, due to an increase in the availability and number of active sites for the hydrolysis of cellulose. However, when the loading of MLC-SO₃H was further increased to 100 wt%, the yield of TRS rapidly decreased to 52.9%, which was caused by too many active sites. Moreover, it is concluded that the increase of MLC-SO₃H loading in a certain scope not only promoted the hydrolysis of cellulose but also facilitated the formation of reducing sugars. Once the loading of MLC-SO₃H exceeded a critical value, the excessive MLC-SO₃H would not only accelerate the occurrence of side reactions but also increase the production costs of reducing sugars. Hence, 40 wt% MLC-SO₃H loading was chosen in the present work. Furthermore, MLC-SO₃H in the presence of [BMIM]Cl

is effective for the hydrolysis of cellulose (Table 2), and TRS yield under the selected reaction conditions is comparable to that in the previous studies [32,34,48-52].

5. Effect of Water Content

It is common knowledge that water is a necessary reactant in the hydrolysis of cellulose and it can also affect the solubility of cellulose in [BMIM]Cl. To better understand the effect of water on the hydrolysis of cellulose, various water content was investigated in [BMIM]Cl. As indicated in Fig. 4, the yield of TRS with 22.1% was still obtained without the addition of water; this may be ascribed to the hygroscopicity of [BMIM]Cl and cellulose. In other words, [BMIM]Cl and cellulose were prone to absorb some moisture in the process of operation, which would promote the hydrolysis of cellulose. Moreover, when 1 wt% water was added into [BMIM]Cl, TRS yield dramatically increased to 69.3%. However, when water content was increased from 2 to 10 wt%, the yield of TRS quickly decreased from 63.6 to 41.7%. The explanation for this trend is that a small amount of water could lower the viscosity of [BMIM]Cl and then promote the mass transfer between catalyst and cellulose, which helps the hydrolysis of cellulose. However, a large amount of water could decrease the solubility of cellulose in [BMIM]Cl, even leading to the precipitation of cellulose from [BMIM]Cl, which is negative for the hydrolysis of cellulose. In conclusion, water plays an important role in the hydrolysis of cellulose and its content should be carefully controlled to obtain a higher yield of TRS.

6. Recycling of Catalyst

The recyclability of catalyst is extremely important in evaluating the efficiency of catalyst, which is beneficial to reducing the cost of practical production in the hydrolysis of cellulose. In the present work, 10 mL deionized water was first added to the reaction mixture to decrease the viscosity of [BMIM]Cl after each reaction run. Subsequently, the used MLC-SO₃H could be readily separated from the reaction mixture with an external magnet (Fig. 5). After separation, MLC-SO₃H was repeatedly washed six times with deionized water and dried in a vacuum oven at 65 °C for 12 h. Then, the recovered MLC-SO₃H was directly added into fresh [BMIM]Cl and used for the next reaction run under the same reaction conditions. As depicted in Fig. 6, no obvious decrease in catalytic activity was observed after five successive reaction runs. The yield of TRS was still more than 64.3%, suggesting that MLC-SO₃H exhib-

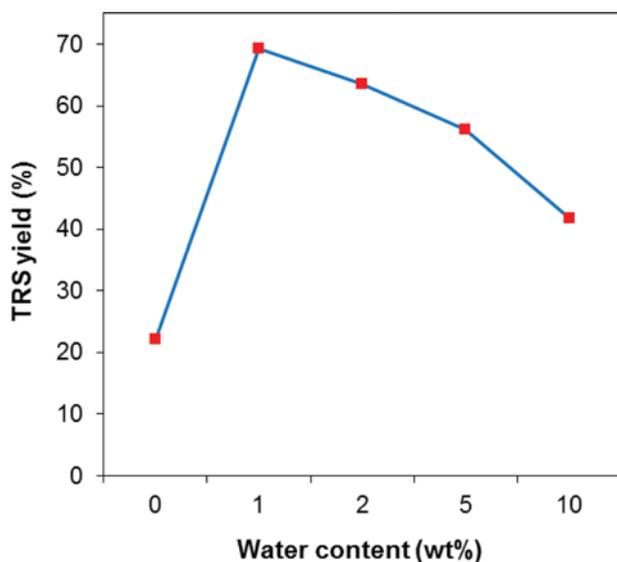


Fig. 4. Effect of water content on the hydrolysis of cellulose. Reaction conditions: 50 mg cellulose, 20 mg MLC-SO₃H, 1 g [BMIM]Cl, 140 °C, 150 min. Note: water content is relative to the mass of [BMIM]Cl.



Fig. 5. Separation of MLC-SO₃H with an external magnet.

ited excellent catalytic stability and recyclability. Moreover, it is particularly necessary to point out that the density of -SO₃H groups on the used MLC-SO₃H after five successive reaction runs was measured to be 0.74 mmol·g⁻¹, which is almost the same to 0.77 mmol·g⁻¹ on the fresh MLC-SO₃H, indicating that -SO₃H groups were hardly leached. Therefore, the slight decrease of TRS yield in the fifth reaction run should be due to the mass loss of MLC-SO₃H in the washing step. In addition, MLC-SO₃H possessed a porous structure with a high surface area, so it was likely to adsorb some insoluble humins formed in the hydrolysis of cellulose and then block the active sites on catalyst and suppress the formation of reducing sugars to a certain extent, which may be another reason for the slight decrease of TRS yield in the fifth reaction run.

7. Plausible Mechanism for the Hydrolysis of Cellulose over MLC-SO₃H in [BMIM]Cl

According to the above results and the reported literature [15, 38,48,49], the plausible mechanism for the hydrolysis of cellulose

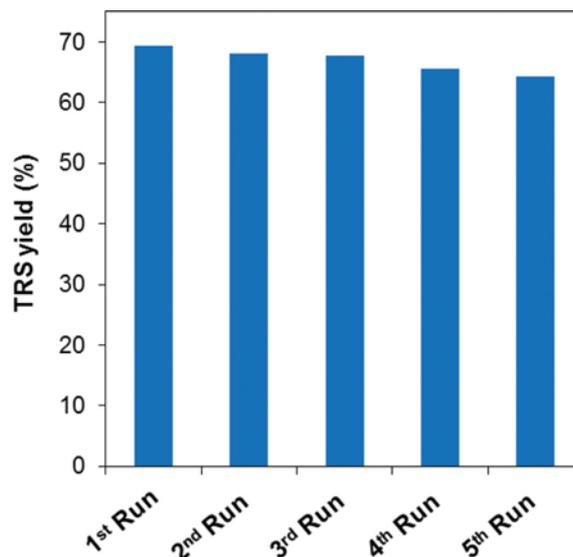
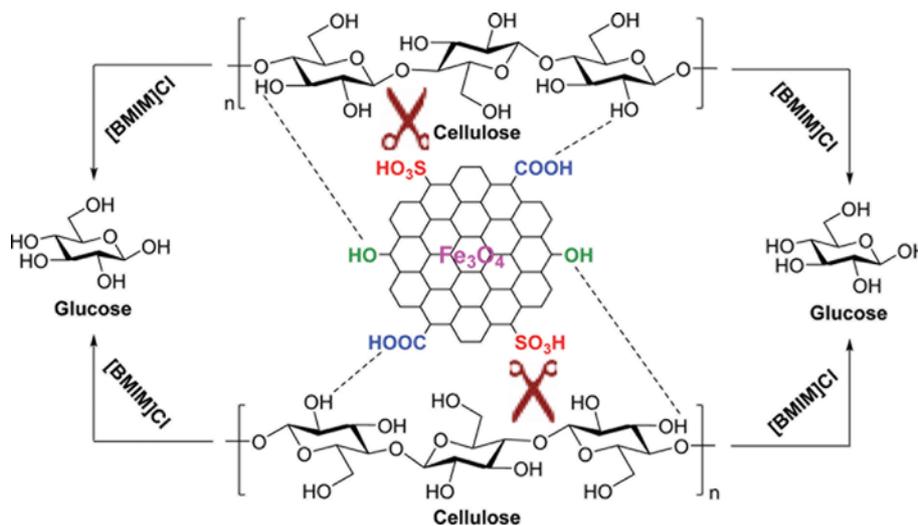


Fig. 6. Recycling of MLC-SO₃H. Reaction conditions: 50 mg cellulose, 20 mg MLC-SO₃H, 0.01 g water, 1 g [BMIM]Cl, 140 °C, 150 min.

over the catalyst of MLC-SO₃H in the presence of [BMIM]Cl was proposed and illustrated in Scheme 1. Initially, cellulose was dissolved into [BMIM]Cl through the formation of competitive hydrogen bonds between -OH groups of cellulose and Cl⁻ of [BMIM]Cl that could disrupt the intramolecular and intermolecular hydrogen bonds in cellulose. Subsequently, cellulose was adsorbed on the surface of MLC-SO₃H by -COOH and phenolic -OH groups via hydrogen-bonding interactions with -OH groups of cellulose. Eventually, β-1,4-glycosidic bonds in cellulose was attacked by -SO₃H groups on MLC-SO₃H and then hydrolyzed into glucose or other reducing sugars. Furthermore, [BMIM]Cl and MLC-SO₃H were of importance for the hydrolysis of cellulose in the above proposed mechanism, because (i) [BMIM]Cl could completely dissolve cellulose to generate a homogeneous solution [25], increasing the opportunity of cellulose to contact the active sites of MLC-SO₃H;



Scheme 1. Plausible mechanism for the hydrolysis of cellulose over a catalyst of MLC-SO₃H in the presence of [BMIM]Cl.

(ii) The adsorption of -COOH and phenolic -OH groups to cellulose could reduce the activation energy in the breakage of β -1,4-glycosidic bonds by -SO₃H groups on MLC-SO₃H [29], lowering the physical barrier in the hydrolysis of cellulose.

CONCLUSIONS

MLC-SO₃H, a magnetic lignin-derived solid acid catalyst with a porous structure and high surface area, was successfully employed for the hydrolysis of cellulose, and a high yield of TRS with 69.3% was achieved in the presence of [BMIM]Cl at a relatively moderate temperature of 140 °C for 150 min. Moreover, MLC-SO₃H could be magnetically separated from the reaction mixture, and when it was used five successive runs, no significant loss in its catalytic activity was observed. Furthermore, a plausible mechanism for the hydrolysis of cellulose in the presence of [BMIM]Cl over a catalyst of MLC-SO₃H was also proposed.

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