




Cite this: *RSC Adv.*, 2018, 8, 41776

Received 6th November 2018  
 Accepted 8th December 2018

DOI: 10.1039/c8ra09190k

[rsc.li/rsc-advances](http://rsc.li/rsc-advances)

## Influence of the acidity of solid catalyst HSO<sub>3</sub>-ZSM-5 on the hydrolysis of pretreated corncob†

Nguyen Hoang Chung,<sup>a</sup> Le Quang Dien,<sup>a</sup> Thai Dinh Cuong,<sup>a</sup> Nguyen Van Lieu<sup>b</sup> and Phan Huy Hoang \*<sup>a</sup>

This work aimed to investigate the application of a solid acid catalyst, a replacement for mineral acids or enzymes, to biomass conversion for further applications. Sulfonated zeolite, HSO<sub>3</sub>-ZSM-5, was successfully synthesized and characterized by several analysis techniques. The obtained catalyst showed high activity and efficiency in the hydrolysis of pretreated corn cob. Moreover, the acidity of the zeolite product positively influenced the biomass conversion. The influences of reaction parameters such as catalyst loading, reaction time and temperature on the hydrolysis were also established. Under suitable conditions, a hydrolysis yield of ~54% was achieved. This recyclable solid acid catalyst provided a promising potential for applications in many industrially important hydrolysis processes of biomass.

### Introduction

Catalysts are generally classified into two classes. Homogeneous catalysts possess many advantages including high activity and great ability to diffuse in solutions. However, they also have many drawbacks such as difficulties in separation and recovery, corrosion hazards, severe reaction conditions, and environmental pollution. Using heterogeneous catalysts, which are recyclable at low energy consumption can be considered as a move toward a more environmentally sustainable process.<sup>1–5</sup>

In the class of heterogeneous catalysts, zeolite materials have been studied and applied widely in many applications. Possessing many advantages such as high surface area, low-toxicity, and functional groups for grafting or attachment, zeolites have been used effectively in industry as ion exchangers, adsorbents, separators, and catalysts for chemical reactions.<sup>6–8</sup> Among a variety of zeolites, ZSM-5 has been used most popularly. On the one hand, the material has strong acidity, high selectivity thanks to its special micro-meso porous structure. On the other hand, ZSM-5 is able to change its acidity and active site. The material, therefore, has become an effective catalyst, which is favorable for organic chemical conversions.<sup>9,10</sup> Catalytic properties strongly depend on acidity and particles size of zeolites. It is well-known that zeolite acidity is reflected by the quantity and strength of active sites. Therefore, catalytic activity and selectivity of a zeolite can be enhanced by improving its acidity. This can be done by introducing functional groups to the structure of

zeolite including surfaces and pores.<sup>11–13</sup> The modified zeolites then show better catalytic activity, acidity, and selectivity in a series of importantly industrial reactions and processes. Yeong *et al.*<sup>11</sup> successfully introduced 3-mercaptopropyl-trimethoxysilane into the silicalite-1 pore-structure by using *in situ* deposition method and subsequently oxidized to sulfonic acid silicalite-1 membrane. The sulfonated silicalite-1 membrane was acting as a membrane with high selectivity and applicable to combined separation and reaction processes. Felice *et al.* synthesized faujasites with sulfonic groups attached, then applied it for water/methanol sorption and proton conductivity.<sup>12</sup> The material showed increased proton conductivity and high selectivity in water/methanol sorption. It, therefore, can be concluded that functionalization of zeolites, especially with sulfonic groups would enhance several properties such as selectivity and catalytic activity. However, there has not been any publication regarding the application of sulfonation of ZSM-5 zeolite catalyst for biomass hydrolysis yet.

Energy demand has been raising rapidly, while traditional natural resources are becoming exhausted. Facing this urgent circumstance, biomass can be considered as a sustainable alternative source, which is also environmentally friendly, for energy.<sup>2,5</sup> Recently, there have been many efforts focusing on the use of catalysts and solvents to improve the efficiency in hydrolysis and/or conversion of lignocellulosic biomass. Zhang *et al.*<sup>14</sup> have successfully produced heteromolybdenic acid-based catalysts, which effectively hydrolyzed and converted cellulose into glycolic acid. Heterogeneous cesium hydrogen phosphotungstate-supported Au catalyst (Au/Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub>) developed by Zhang *et al.*<sup>15</sup> showed high selectivity in the hydrolysis and conversion of cellulose into gluconic acid. In another work,<sup>16</sup> it was able to transform raw biomass to over 67% of formic acid by using Keggin-type vanadium-substituted

<sup>a</sup>School of Chemical Engineering, Hanoi University of Science & Technology, No. 1, Dai Co Viet Street, Hanoi, Vietnam. E-mail: [hoang.phanhuy@hust.edu.vn](mailto:hoang.phanhuy@hust.edu.vn); Tel: +84-4-38684955

<sup>b</sup>Vietnam Institute for Building Materials, 235, Nguyen Trai Street, Hanoi, Vietnam

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ra09190k



phosphomolybdic acid catalyst. Among a variety of solid acid catalysts, sulfonated solid catalyst has also been studied widely.<sup>2,3,5,17–24</sup> For examples, Akiyama *et al.*<sup>2</sup> has successfully synthesized a polymer attached with porous sulfonic acid groups and applied it for cellulose hydrolysis reactions. The new catalyst possessed good resistance to vapor at high temperature; high acidity for the cellulose hydrolysis. Furthermore, Onda *et al.*<sup>18</sup> showed potential results in the hydrolysis of cellulose to glucose using solid acid catalyst. Saw dust, a biomass residue, was used by Liu *et al.*<sup>20</sup> as a carbon source for production of solid acid catalyst based on magnetic porous carbon by a combination of pyrolysis and sulfonation. Their obtained catalyst showed high catalytic activity in sugar hydrolysis.

This work aims to apply sulfonated ZSM-5 zeolite catalyst for hydrolysis reaction of lignocellulosic biomass. Influences of acidity of the HSO<sub>3</sub>-ZSM-5 on efficiency of the biomass hydrolysis are evaluated. Furthermore, other factors affecting the lignocellulose hydrolysis yield including reaction time and temperature are also investigated. The synthesized HSO<sub>3</sub>-ZSM-5 zeolite shows high acidity and catalytic activity in the biomass hydrolysis. These outstanding properties are achieved thanks to the zeolitic structure itself as well as strong sulfonic acid groups that are introduced by sulfonation.

## Experimental

### Materials

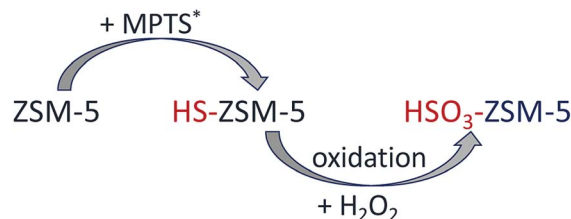
Used chemicals were all analytical grades originated from Sigma-Aldrich including tetraethyl orthosilicate (TEOS); tetra propyl ammonium hydroxide (TPAOH); potassium hydroxide (KOH); sodium aluminate (NaAlO<sub>2</sub>); cetyltrimethyl ammonium bromide (CTAB – C<sub>19</sub>H<sub>42</sub>BrN); 3-mercaptopropyl trimethoxysilane (MPTS); hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).

Dry corncob collected from the North of Vietnam was used for preparation of biomass feedstock. The corncob was subject to ethanol extraction following the procedure described in T 204 cm-97 TAPPI standard. The extraction lasted for 6 h to ensure that all extractives were dissolved and removed. The pretreated corncob was stored at room temperature for further investigations.

### Synthesis of sulfonated zeolite HSO<sub>3</sub>-ZSM-5

ZSM-5 zeolite was synthesized by using templating agents according to Hoang *et al.*<sup>8</sup> In addition, cetyl trimethylammonium bromide (CTAB – C<sub>19</sub>H<sub>42</sub>BrN) was used as a surfactant to obtain mesoporous structure of zeolite. The resulted ZSM-5 was then subject to –HS attachment reaction before oxidizing these –HS groups to –HSO<sub>3</sub> in the final product. The synthesis consists of two stages as described in Scheme 1.

**Stage 1.** A specific amount of the zeolite (*m*<sub>z</sub>) was weighed and placed in a beaker. MPTS was added at different mass ratios of zeolite and MPTS of 1 : 1.5, 1 : 2, 1 : 2.5, and 1 : 3. Toluene was used as a solvent. The mixtures were then heated and stirred within 6 h. After this time, the solid part was separated from the liquid phase by centrifugation. It was then washed for several times with ethanol and distilled water or until the



Scheme 1 Two-stage process for synthesis of HSO<sub>3</sub>-ZSM-5.

catalyst gained its white color. Finally, the catalyst was dried at 90 °C to remove all the remaining water.

**Stage 2.** The catalyst with –HS groups in the structure was oxidized using H<sub>2</sub>O<sub>2</sub> (30 wt%) with solid/liquid ratio of 1/10. The reaction was conducted at room temperature for approx. 12–15 h with continuous stirring. Subsequently, the mixture was centrifuged and washed with distilled water for 3–4 times before drying at 90 °C till constant weight. Final product was a sulfonated zeolite.<sup>12</sup>

### Biomass hydrolysis catalyzed by HSO<sub>3</sub>-ZSM-5 zeolite

The hydrolysis was conducted in a 150 mL autoclave reactor. 0.5 g of pretreated corncob was weighed and placed in the reactor. A certain amount of the catalyst and water were added to reach desired solid/liquid ratios. The reactor was placed in an oil bath, which was set at 100–130 °C and maintained at the reaction temperature for a certain period (4–8 h).

After the hydrolysis, the reactor was cooled down to room temperature, and then the hydrolysate was separated from reaction mixture using filter papers. Reducing sugars of the hydrolysate were analyzed with HPLC. The solid residue was washed, dried for determination of dry yield of the hydrolysis.

### Structural characterizations

X-ray diffraction (XRD) patterns of all samples were recorded with a D8-Advance X-ray Diffractometer equipped with a scintillation counter detector with Cu-K $\alpha$  radiation. Other parameters were wavelength  $k = 1.5406 \text{ \AA}$ , voltage 30 kV, current intensity 25 mA, scanning angle  $2\theta$  changed from 5° to 50°, scanning rate 2° min<sup>-1</sup>, room temperature 25 °C. Scanning electron microscope/energy dispersive X-ray spectroscopy (SEM-EDS) were performed with FE-SEM JEOL JSM-7600F (Japan). Sample was subject to several steps of preparation including dispersion in ethanol, drying, coating onto sample holder, coating with a very thin layer of gold onto surface. Infrared spectra (IR) of samples were recorded with an FTIR NICOLET 6700 NRX RAMAN MODULE – THERMO using KBr pellet method (1 mg of sample per 100 mg of KBr). Brunauer–Emmett–Teller (BET) analysis using a Quantachrome NOVA 4200 E Porosimeter analyzer was used to determine mesoporous properties of the samples. NH<sub>3</sub>-temperature programmed desorption (TPD) was used to determine the amount and strength of the acid sites with Micrometrics 2900 instrument with a thermal conductivity detector. Approx. 0.20 g of sample was saturated with NH<sub>3</sub> at 120 °C, then flushed with helium to remove all physically adsorbed NH<sub>3</sub>. Finally, the



desorption of  $\text{NH}_3$  was carried out at temperature ranging from 100 to 550 °C with heating rate of 10 °C  $\text{min}^{-1}$ .

Basic components of the pretreated corncob were characterized following TAPPI methods.

After the hydrolysis reaction, the hydrolysate was centrifuged to recover the supernatant. Total reducing sugars (TRS) were analyzed with an HPLC (High Performance Liquid Chromatography) Agilent 1200 equipped with G1322A vacuum pump, Aminex HPX-87P column. Working conditions were controlled as follows: temperature 5–50 °C, humidity 5–96%, and using GLP/GMP compliance as standard. The stationary phase was in lead form with particle size of 9  $\mu\text{m}$ , 8% cross linkage; mobile phase was ionized water which was filtered through a 0.45  $\mu\text{m}$  filter and degassed, working well at pH 5–9. Obtained data were analyzed with Agilent 2D LC ChemStation software (G2170BA). The measurements were conducted at the Laboratory of Food Technology (Hanoi University of Science and Technology).

## Results and discussion

### Synthesis and characterization of solid acid catalysts $\text{HSO}_3\text{-ZSM-5}$ with different acidity

Mesoporous ZSM-5 zeolite was synthesized by a hydrothermal method and then the obtained zeolite was subject to a 2-phase reaction to attach  $\text{HSO}_3^-$  onto its structure. The reaction resulted in a sulfonated zeolite ( $\text{HSO}_3\text{-ZSM-5}$ ), whose structure was characterized by XRD, IR spectroscopy, while EDS technique helped confirm the presence of  $\text{HSO}_3$  groups based on S content of the zeolite. XRD patterns (Fig. S1, ESI<sup>†</sup>) of the mesoporous  $\text{HSO}_3\text{-ZSM-5}$  zeolite particles show an MFI-type zeolitic structure with high crystallinity and well-defined diffraction peaks of a high structural order. The as-obtained  $\text{HSO}_3\text{-ZSM-5}$  particles after the sulfonation are pure without any other non-zeolitic phases as seen from the XRD pattern. There are almost no alterations on structure and crystallinities of the zeolite as confirmed by XRD characterization.

According to the IR spectra (Fig. 1), the sample possesses all specific vibration spectra of a zeolite structure. The broad peak at around 3440  $\text{cm}^{-1}$  is OH stretching of water while the peak at around 1635  $\text{cm}^{-1}$  is bending mode of OH of water absorbed

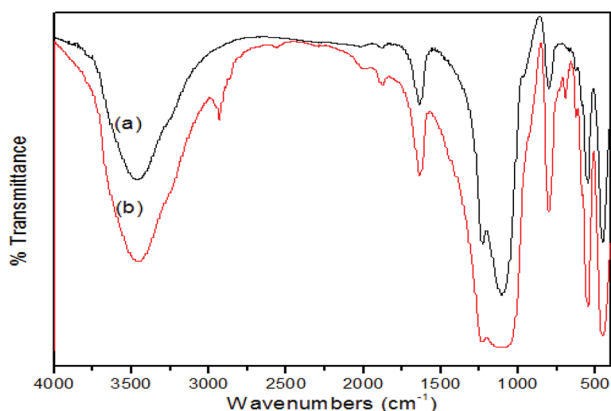


Fig. 1 IR spectra of (a) ZSM-5 zeolite and (b)  $\text{HSO}_3\text{-ZSM-5}$  zeolite.

in the channels of zeolites.<sup>10</sup> The asymmetric stretching of Si–O–Si or Si–O–Al bonds with frequency band at 1099  $\text{cm}^{-1}$ , the most prominent in the IR spectra is also observed.<sup>8</sup> In addition, the band observed at around 450  $\text{cm}^{-1}$  and at 550  $\text{cm}^{-1}$  are assigned to internal vibrations of TO (tetrahedrons) and vibrations of the secondary building units, respectively.<sup>8</sup> As seen in Fig. 1B, there are extra new peaks with broadband around 2400–2900  $\text{cm}^{-1}$  assignable to the strong hydrogen bond between  $\text{SO}_3\text{H}$  groups<sup>1</sup> and new peaks at around 1050  $\text{cm}^{-1}$  and 650  $\text{cm}^{-1}$  which is assigned to S=O symmetric stretching and S–O stretching, respectively.<sup>12</sup> This proves that sulfonic groups were successfully introduced into the surfaces of the ZSM-5 zeolite forming  $\text{HSO}_3\text{-ZSM-5}$ .

These results are once again confirmed by EDS data as shown in Fig. 2. According to Fig. 2(A), 0.5% of S is present in the sample, while no S is detected in the non-modified zeolite (data not shown). Even distribution of all elements, especially S observed in Fig. 2(B) indicates that S has been successfully and effectively introduced to the zeolite structure with high dispersion (Fig. 2, B3).

$\text{N}_2$  adsorption and desorption isotherms of the  $\text{HSO}_3\text{-ZSM-5}$  zeolite (Fig. S2, ESI<sup>†</sup>) indicate a relatively large diameter of the

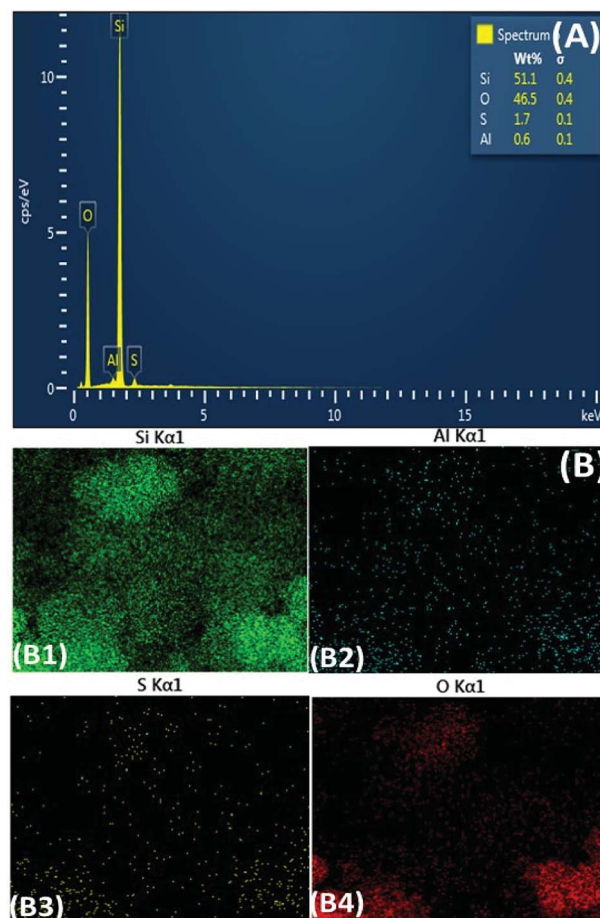


Fig. 2 Elemental compositions (A) and distribution (B) of  $\text{HSO}_3\text{-ZSM-5}$  zeolite sample by EDS analysis, where (B1) Si element, (B2) Al element, (B3) S element and (B4) O element (the sample was treated at 60 °C for 6 h, at MPTS : zeolite ratio of 2.5 : 1).



mesopore. The BET surface area and pore diameter of the HSO<sub>3</sub>-ZSM-5 zeolite (468 m<sup>2</sup> g<sup>-1</sup> and 5.6 nm, respectively) are slightly lower than those of the non-modified ZSM-5 zeolite (487 m<sup>2</sup> g<sup>-1</sup> and 5.8 nm, respectively). This suggests that the bulky sulfonic groups are successfully incorporated on the HSO<sub>3</sub>-ZSM-5 pore surface and they do not change the pore structure of the zeolite.

### Effect of sulfonation temperature

Temperature mainly influences any chemical process. In this work, influence of temperature of the sulfonation was investigated by changing the treatment temperature while maintaining other conditions. The obtained product, HSO<sub>3</sub>-ZSM-5, was elementally analyzed using energy-dispersive X-ray spectroscopy (EDS) for determination of S (in HSO<sub>3</sub>) attached on ZSM-5 particles. On the other hand, NH<sub>3</sub>-TPD was utilized to investigate the concentration and strength of acid sites by the amount of desorbed NH<sub>3</sub> and the location of desorption peak. The results are presented in Table 1.

According to the results shown in Table 1, when increasing temperature from 50 °C to 60 °C, sulfur content in the product is enhanced from 0.1% to 0.6%, respectively. This is obvious since increased temperature supports the reaction making more MPTS attached on the zeolite surfaces. However, when temperature reaches 70 °C, S content reduces to 0.5%. This can be explained by the fact that high temperature causes solvent (toluene) to evaporate, which does not favor the reaction by reducing the contact of the agent to the zeolite surfaces. Suitable reaction temperature is, therefore, chosen at 60 °C. On the other hand, the acidity is directly proportional to the amount of HSO<sub>3</sub> groups, which is reflected in S content. The highest acidity of 1.52 mmol g<sup>-1</sup> is obtained when conducting the synthesis at 60 °C. Lower or higher temperature leads to reduction in this parameter. Sample M2 was, therefore, chosen for further investigation.

### Effect of MPTS amount

Influences of MPTS dosages on the sulfonation was also investigated by adjusting the amount of MPTS used while other conditions were kept constant. For this purpose, M2 sample obtained from the previous section was subject to sulfonation using different MPTS : zeolite ratios. The processes resulted in corresponding products namely M2-1, M2-2, M2-3, and M2-4. Table 2 presents S content in correlation with MPTS amount of samples.

As seen from Table 2, increasing MPTS dosage, *i.e.* MPTS : zeolite ratio, results in a significant enhancement of S

**Table 2** Influence of MPTS dosage on sulfur content and on acidity of the HSO<sub>3</sub>-ZSM-5 zeolite (reaction time and temperature were 6 h and 60 °C, respectively)

Sample	MPTS : zeolite mass ratio	S content, %	Acidity, mmol g <sup>-1</sup>
M2	1 : 1	0.6 ± 0.05	1.52
M2-1	1.5 : 1	0.9 ± 0.05	1.87
M2-2	2 : 1	1.2 ± 0.05	2.13
M2-3	2.5 : 1	1.7 ± 0.05	2.89
M2-4	3 : 1	1.4 ± 0.05	2.45

content of the HSO<sub>3</sub>-ZSM-5. When using the same amount of MPTS and zeolite (1 : 1 ratio), S content of the product is approx. 0.6%. Doubling the MPTS amount, *i.e.* 2 : 1 ratio, the content of this element rises to 1.2%. S content of the HSO<sub>3</sub>-ZSM-5 zeolite reaches its highest value of 1.7% when the amount of MPTS is 2.5 times greater than the zeolite. This can be explained based on a well-known theory of reaction dynamics, which states that concentration of a reactant (*i.e.* dosage) is directly proportional to reaction rate as well as efficiency of the reaction. However, when the ratio is 3 : 1, S content reduces to 1.6%. This indicates that the amount of S in the zeolite may reach a saturation level. Once this state is reached, more reactant added will not provide any enhancement to S content in the zeolite. On the other hand, this sometimes might create negative effect.

The dependency of the HSO<sub>3</sub>-ZSM-5 acidity on S content is once again confirmed. The acidity is directly proportional to S content in the zeolite and reaches its highest value of 2.89 mmol g<sup>-1</sup> at the MPTS : zeolite ratio of 2.5 : 1.

### Lignocellulose hydrolysis

HSO<sub>3</sub>-ZSM-5 zeolite catalysts with different contents of sulfonic group corresponding to different acidities were selected to investigate their influences on biomass hydrolysis. The pre-treated corncob containing of 30.1% of cellulose, 38.6% of pentosan, and 19.3% of lignin was used as lignocellulosic biomass in the hydrolysis experiment. The results regarding S content and yield of reducing sugar are presented in Table 3.

According to Table 3, sulfur content (*i.e.* the amount of HSO<sub>3</sub> groups attached to the ZSM-5 zeolite particles) clearly affects the hydrolysis yield. When S content of the catalyst increases from 0.6% to 1.7%, the yield of reducing sugars also increases from 49.4% to 54.1%, respectively. The reducing sugar yield reaches its highest value of 54.1% when S content is 1.7%. This is obvious since S content is directly proportional to the amount of HSO<sub>3</sub> groups attached to the ZSM-5 particles, which improves acidity of the sulfonated catalyst. As a result, the hydrolysis of glycosidic linkages in the lignocellulosic material is improved significantly. Sample M2-3 with 1.7% of S

**Table 1** Sulfur content of the obtained zeolite HSO<sub>3</sub>-ZSM-5 (MPTS : zeolite mass ratio was 1 : 1 and reaction time was 6 h)

Sample	Temperature, °C	S content, %	Acidity, mmol g <sup>-1</sup>
M1	50	0.1	0.66
M2	60	0.6	1.52
M3	70	0.5	1.40

**Table 3** Sulfur content of synthesized catalyst samples and correlative yield of reducing sugar

Catalyst sample code	M2	M2-1	M2-2	M2-3	M2-4
S content, %	0.6	0.9	1.2	1.7	1.4
Reducing sugar yield, %	49.3	51.4	52.8	54.1	53.2



was, therefore, selected as the catalyst for hydrolyzing the biomass in further investigations.

In order to investigate the effect of catalyst loading on the yield of reducing sugar, three experiments were carried out at three catalyst : biomass ratios of 0.5 : 1, 1 : 1, and 1.5 : 1. The obtained results show that the higher loading of catalyst the higher reducing sugar yield could be achieved. In particular, the yield of sugar is 38.9%, 54.1%, and 55.0%, respectively. When increasing the amount of catalyst from 1 : 1 to 1.5 : 1 ratio, the yield of sugar is slightly increased. However, due to economic issues, 1 : 1 ratio of catalyst loading is chosen for next experiments. Moreover, two reactions were carried out under similar reaction conditions for comparison: one without catalyst and one with parent ZSM-5 zeolite catalyst. The results show that only a small amount of the corncob is hydrolyzed in the absence of catalyst as well as in presence of parent ZSM-5 zeolite. When using original ZSM-5 catalyst, ~19% of reducing sugars are achieved. Without catalyst, the corncob biomass is partly hydrolyzed (about 8% of reducing sugars are obtained) due to dissolution of low molecular weight hemicelluloses.

Normally, temperature positively affects reaction yield as increased temperature results in increased reaction rate. In this work, influences of reaction temperature of the corncob hydrolysis producing single sugars was also studied. The results are illustrated in Fig. 3.

As can be seen from Fig. 3, when increasing temperature from 100 °C to 130 °C, the reducing sugar yield increases from 19.3% to 54.9%. The highest yield of reducing sugar is 54.9% when conducting the reaction at 130 °C. However, when temperature is increased for 10 °C from 120 to 130 °C, the yield of reducing sugar only enhances from 54.1% to 54.9%, *i.e.* approx. 0.8%. Based on economic benefits and technical issues, 120 °C was chosen as an appropriate temperature for the hydrolysis of the corn cob catalyzed by the synthesized HSO<sub>3</sub>-ZSM-5.

Reaction time is one of important factors that affects any chemical process. To investigate the influences of reaction time on the reducing sugar yield of the biomass hydrolysis, the reaction time was varied from 4 to 8 h. According to the results illustrated in Fig. 4, the reducing sugar yield is almost

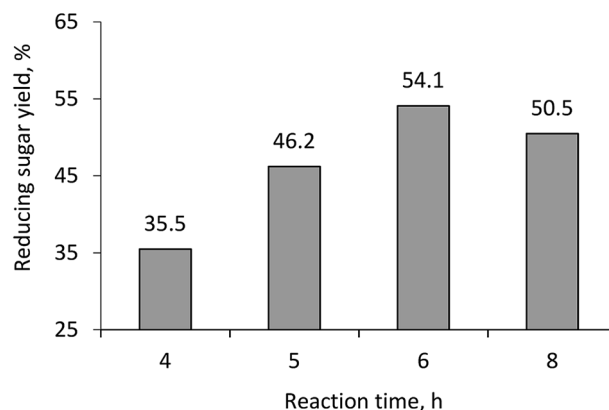


Fig. 4 Influence of reaction time on reducing sugar yield.

proportional to the time when other conditions such as temperature, catalyst dosage and solid/liquid ratio were kept constant. The yield corresponding to the time of 4, 5, and 6 h were 35.5, 46.2, 54.1%, respectively. However, when the hydrolysis was conducted for longer time of 8 h, the yield tends to slightly decrease from 54.1% to 50.5%. It can be explained by the fact that the reducing sugars are partly degraded and converted into other substances when lengthening the reaction time.<sup>18</sup> Therefore, 6 h was chosen as suitable reaction time for the hydrolysis.

Interestingly, besides glucose, xylose and arabinose were also obtained after the hydrolysis of corncob biomass. It can be explained that hemicellulose of corncob contains various polysaccharides such as xylan and arabinan. Under conditions of temperature: 120 °C; time: 6 h; and catalyst : biomass ratio: 1 : 1, the yield of glucose, xylose and arabinose in reducing sugars was determined as 23, 28.7 and 2.4%, respectively.

Furthermore, sample M2-3 was subject to several runs of biomass hydrolysis to evaluate its recycling ability. Results (Fig. 5) show that after the sixth run, the obtained amount of reducing sugars is about 52%, quite close to the first run with about 54% of reducing sugars. This indicates that the synthesized catalyst can be recycled for several times without losing its catalytic activity.

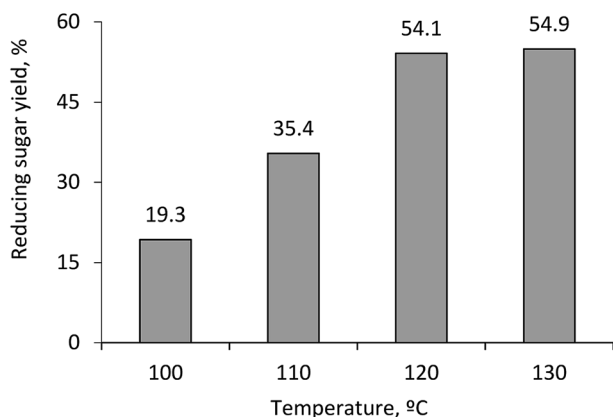


Fig. 3 Influence of reaction temperature on reducing sugar yield.

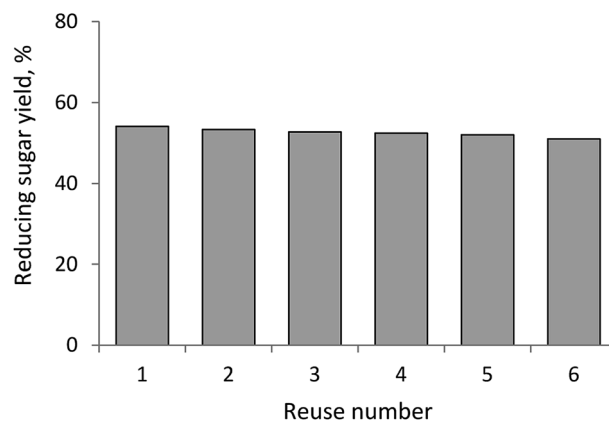


Fig. 5 Reuse of sulfonated ZSM-5 zeolite catalyst in hydrolysis of pre-treated corn-cob.



## Conclusions

In processing of lignocellulosic materials for production of valuable products, the hydrolysis of carbohydrates such as cellulose, hemicelluloses forming monosaccharides or single sugars is regarded as a necessary first step. The single sugars can be further catalytically converted into a variety of intermediates, chemicals, and fuels. In this work, solid acid catalyst as an alternative to mineral acids or enzymes in biomass conversions was studied. HSO<sub>3</sub>-ZSM-5 was successfully synthesized by sulfonation of ZSM-5 zeolite catalyst and applied to the hydrolysis of pretreated corn cob. The obtained solid acid catalyst shows high catalytic activity and effectively influences the biomass hydrolysis. Furthermore, proper conditions for the hydrolysis using HSO<sub>3</sub>-ZSM-5 as catalyst have been established as temperature: 120 °C; time: 6 h; solid/liquid ratio: 1/20; catalyst dosage: 1 : 1. Under these conditions, the yield of reducing sugars of the hydrolysis catalyzed by HSO<sub>3</sub>-ZSM-5 is ~54%. The as-synthesized catalyst, which is a recyclable solid acid catalyst provides a promising potential for applications in many industrially important hydrolysis processes of biomass.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.03-2015.15.

## Notes and references

- 1 S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi and M. Hara, *J. Am. Chem. Soc.*, 2008, **130**, 12787.
- 2 G. Akiyama, R. Matsuda, H. Sato, M. Takata and S. Kitagawa, *Adv. Mater.*, 2011, **23**, 3294.
- 3 S. Van de Vyver, L. Peng, J. Geboers, H. Schepers, F. de Clippel, C. J. Gommès, B. Goderis, P. A. Jacobs and B. F. Sels, *Green Chem.*, 2010, **12**, 1560.
- 4 J. Pang, A. Wang, M. Zheng and T. Zhang, *Chem. Commun.*, 2010, **46**, 6935.
- 5 D. Lai, L. Deng, Q. Guo and Y. Fu, *Energy Environ. Sci.*, 2011, **4**, 3552.
- 6 P. H. Hoang and L. Q. Dien, *Chem. Eng. J.*, 2015, **262**, 140.
- 7 P. H. Hoang and B. Nguyen Xuan, *RSC Adv.*, 2015, **5**, 78441.
- 8 P. H. Hoang, N. T. Nhung and L. Q. Dien, *AIP Adv.*, 2017, **7**, 105311.
- 9 P. H. Hoang and N. V. Long, *Cellul. Chem. Technol.*, 2017, **51**, 447.
- 10 G. Giannetto, *et al.*, *Zeolites*, 1997, **19**, 169.
- 11 Y. F. Yeong, A. Z. Abdullah, A. L. Ahmad and S. Bhatia, *J. Eng. Sci. Technol.*, 2008, **3**, 87.
- 12 V. Felice, S. Ntais and A. C. Tavares, *Microporous Mesoporous Mater.*, 2013, **169**, 128.
- 13 I. K. Mbaraka, D. R. Radu, V. S. Y. Lin and B. H. Shanks, *J. Catal.*, 2003, **219**, 329.
- 14 J. Zhang, X. Liu, M. Sun, X. Ma and Y. Han, *ACS Catal.*, 2012, **2**, 1698.
- 15 J. Zhang, X. Liu, M. N. Hedhili, Y. Zhu and Y. Han, *ChemCatChem*, 2011, **3**, 1294.
- 16 J. Zhang, M. Sun, X. Liu and Y. Han, *Catal. Today*, 2014, **233**, 77.
- 17 M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri and K. Arai, *Ind. Eng. Chem. Res.*, 2000, **39**, 2883.
- 18 A. Onda, T. Ochi and K. Yanagisawa, *Green Chem.*, 2008, **10**, 1033.
- 19 Y. Xiong, Z. Zhang, X. Wang, B. Liu and J. Lin, *Chem. Eng. J.*, 2014, **235**, 349.
- 20 W.-J. Liu, K. Tian, H. Jiang and H.-Q. Yu, *Sci. Rep.*, 2013, **3**, 2419.
- 21 L. Hu, L. Lin, Z. Wu, S. Zhou and S. Liu, *Appl. Catal., B*, 2015, **174–175**, 225.
- 22 M. Goswami, S. Meena, S. Navatha, K. N. Prasanna Rani, A. Pandey, R. K. Sukumaran, R. B. N. Prasad and B. L. A. Prabhavathi Devi, *Bioresour. Technol.*, 2015, **188**, 99.
- 23 F. Guo, Z. Fang, C. C. Xu and R. L. Smith, *Prog. Energy Combust. Sci.*, 2012, **38**, 672.
- 24 S. Morales-delaRosa, J. M. Campos-Martin and J. L. G. Fierro, *Chem. Eng. J.*, 2012, **181–182**, 538.

