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## Selective Dehydration of Sorbitol to 1,4-anhydro-D-sorbitol

### Catalyzed by Polymer-supported Acid Catalyst

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**Abstract:** Novel Polymer-supported Brønsted acid polymer catalysts have been successfully synthesized by radical polymerization, followed by a simple solvothermal route and ion exchange step. The as-synthesized co-polymers were characterized by Elemental Analysis, FT-IR spectroscopy, thermogravimetric analysis and scanning electron microscopy and then were employed as a heterogeneous catalyst for dehydration of sorbitol. Especially, the polymer catalysts have a unique advantage of adjustable Brønsted acidity, and the polymer with  $1.82 \text{ mmol}\cdot\text{g}^{-1}$  of Brønsted acidity was a very efficient catalyst for highly selective dehydration of sorbitol into 1,4-anhydro-D-sorbitol. The dehydration reaction can be completed within 4 h and the selectivity of 1,4-anhydro-D-sorbitol achieved 90%. Moreover, the present catalysts resisted acid-leaching and can be recycled in five consecutive cycles without obvious loss of activity.

**Keywords:** Polymer, Brønsted acid, 1,4-anhydro-D-sorbitol, Sorbitol, Dehydration

## Introduction

The recent developments in the efficiency of the conversion of biomass into chemical materials have been of interest in sustainable chemistry.<sup>1-7</sup> Biomass, which is regarded as a renewable feedstock, has been intensively investigated for the production of fine chemicals and transportation fuels.<sup>8-14</sup> However, selective formation of a sole valuable product from biomass remains still a challenge, because these kinds of reactions are usually accompanied by many side-reactions, producing various undesirable by-products.<sup>8,15,16</sup> Cellulose is a biomass source produced on a massive scale every year, and it can be transformed into glucose and other important derivatives.<sup>17-21</sup> Sorbitol, produced by the hydrogenation of glucose, is one of the top twelve building block chemicals.<sup>22-26</sup> As a platform chemical, it is of considerable importance for the future replacement of fossil-resource-based products and it can be transformed into polyols such as propylene glycol, ethylene glycol and 1,4-anhydro-D-sorbitol and isosorbide.<sup>27</sup> Among these polyol products, 1,4-anhydro-D-sorbitol is an important material for surfactants, emulsifiers, cosmetics, synthetic resins, pesticides, and biologically active substances.<sup>28-31</sup> As a result of the versatile applications of 1,4-anhydro-D-sorbitol, the catalytic synthesis was developed rapidly by the dehydration of sorbitol over the past few years, but sustainable and economically viable routes for its production have not been achieved.

<Insert Scheme1>

Sorbitol dehydration has been studied since the mid-20<sup>th</sup> century.<sup>32</sup> Sorbitol dehydration has been reported early with inorganic acid catalysts, such as sulfuric and hydrochloric acids, in the temperature range 377-408 K,<sup>33,34</sup> and with hydrofluoric acid at 293 K.<sup>34</sup> In these processes, however, a neutralization procedure is essential to remove hazardous inorganic acid catalysts, and also the separation processes of the dehydration products from the salt solutions are troublesome.<sup>32</sup> Therefore, solid acid catalysts, such as ion exchange resin, HY, and H-ZSM-5<sup>36</sup> have attracted much attention and used as potential catalysts for 1,4-anhydro-D-sorbitol formation due to their environmentally friendly nature with respect to lower corrosiveness, less waste and easy separation and recovery. However, the results were not satisfactory due to

the low activity and poor selectivity.

As shown in Scheme 1, 1,4-anhydro-D-sorbitol is obtained by monomolecular dehydration of sorbitol and isosorbide was produced by the stepwise dehydration of 1,4-anhydro-D-sorbitol. Although the 1,4-anhydro-D-sorbitol production from sorbitol proceeds through one-step reaction, many kinds of by-products generated simultaneously. The dehydration step requires a strong acid particularly to activate hydroxyl groups of sorbitol molecules.<sup>32,37</sup> Therefore, a hydrothermally stable solid acid can be an efficient catalyst in the conversion of sorbitol to 1,4-anhydro-D-sorbitol, which is also commonly encountered in the transformation of biomass-derived oxygenated feedstocks. It was worth noting that aqueous-phase dehydration of sorbitol has been normally performed by using homogeneous and heterogeneous acid catalysts. The reaction over solid acids typically occurs at temperatures higher than 473 K.<sup>38</sup> In the view of green chemistry, the process for dehydration of sorbitol under water-free and more mild conditions would be highly promising.

The copolymer showing Brønsted acidity has attracted much attention and was employed for acid catalysis in recent years.<sup>39,40</sup> In this aspect, superhydrophobic nanoporous polydivinylbenzene materials have been synthesized and used for transesterification and dehydration of sorbitol to isosorbide.<sup>41,42</sup> Herewith, we demonstrate a successful preparation of sulfonic group-functionalized, stable nonporous polymer-based acid catalyst. The polymer catalyst exhibits the promising properties such as an adjustable acidity. Especially, the current polymer-based acid catalyst showed much higher catalytic performance for the dehydration of sorbitol to 1,4-anhydro-D-sorbitol, in comparison with conventional acid catalysts such as hydrochloric acid, sulfuric acid and acidic resins. The excellent catalytic activity, product selectivity and recyclability for the polymer-based catalyst may offer a simple and potential route for the preparation of 1,4-anhydro-D-sorbitol from sorbitol.

## Experimental

## Materials

1-vinylimidazole(99%) was supplied from Aldrich. Amberlyst 15 ion exchange resin was supplied from Alfa Aesar. HZSM-5( $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ , molar ratio) was provided by Nankai University, China. Sodium p-styrene sulfonate (1) was purchased from Aladdin Industrial Corporation, China. 1-butyl-3-(3-sulfopropyl) imidazolium hydrogensulfate (IL- $\text{HSO}_4$ ),<sup>43,44</sup> 1-vinyl-3-(3-sulfopropyl) imidazolium (2) and 1-vinyl-3-(3-trimethoxysilyl propyl)-imidazolium chloride (3)<sup>45,46</sup> were synthesized according to the previously reported procedure, respectively. Sorbitol, isosorbide, (3-chloropropyl) trimethoxy-silane,  $\text{H}_2\text{SO}_4$  (96%, GR), 1,3-propanesultone(99.5%), azobisisobutyronitril(AIBN), toluene and tetraethoxysilane (TEOS) (4) were purchased from SCRC (Sinopharm Chemical Reagent Co., Ltd, Shanghai).

## Catalyst preparation

### *Synthesis of IL- $\text{HSO}_4$*

The IL- $\text{HSO}_4$  was synthesized as follows: to a solution of 1,3-propanesultone (150 mmol) dissolved in anhydrous toluene (100 mL) was added 1-butylimidazole (150 mmol), dropwise at 0 °C. The resulting mixture was slowly warmed to room temperature and stirred for 2 h. After completion, the reaction mixture was filtered to obtain the zwitterion as a white solid, which was subsequently washed with diethyl ether ( $3 \times 25$  mL) and dried at room temperature under vacuum for 24 h. To a solution of the zwitterionic intermediate (150 mmol) in deionized water (50 mL), a stoichiometric amount of sulfuric acid was added slowly and the mixture stirred first at room temperature for 30 min, then at 90 °C for 2 h. The resulting solution was concentrated by rotary evaporation then dried at 50 °C under vacuum for 24 h.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ , room temperature):  $\delta = 0.67(\text{t}, 3\text{H}), 1.18(\text{m}, 2\text{H}), 1.62(\text{m}, 2\text{H}), 2.09(\text{m}, 2\text{H}), 2.68(\text{t}, 2\text{H}), 4.03(\text{t}, 2\text{H}), 4.22(\text{t}, 2\text{H}), 4.98(\text{s}, 2\text{H}), 7.27(\text{s}, 1\text{H}), 7.34(\text{s}, 1\text{H}), 8.65(\text{s}, 1\text{H})$ .

### *Synthesis of 2*

Firstly, 1,3-propanesultone (3.50 g, 2.87 mmol) was slowly added to

1-vinylimidazole (2.50 g, 2.65 mmol) in a 50 mL round bottom flask at 0 °C. The mixture was stirred at room temperature for 24 h. Then the resulting solid was washed with ether for three times and dried in vacuum. NMR: <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, room temperature):  $\delta$  = 2.23 (t, 2H), 2.85 (t, 2H), 4.30 (t, 2H), 5.34 (d, 1H), 5.69 (d, 1H), 7.03 (t, 1H), 7.53 (s, 1H), 7.69 (s, 1H), 9.01 (s, 1H).

### *Synthesis of 3*

The synthesis was carried out according to the previous report.<sup>45</sup> (3-chloropropyl)trimethoxysilane (2.00 g, 0.01 mol) and 1-vinylimidazole (0.94 g, 0.01 mol) were mixed in a 50 mL stainless steel autoclave reactor and the system was purged with nitrogen for three times. The mixture was stirred at 90 °C for 60 h under nitrogen atmosphere. The reaction mixture was cooled down, washed with ether for three times and dried in vacuum. The remaining volatile substances were removed under reduced pressure. The oily product was obtained with 90% yield. This viscous oil was used immediately in the next step. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, room temperature):  $\delta$  = 7.66 (s, 1H), 7.47 (s, 1H), 7.01 (t, 1H), 5.67 (d, 1H), 5.32 (d, 1H), 4.12 (s, 2H), 3.16 (s, 9H), 1.88 (s, 2H), 0.50 (s, 2H).

### *The synthesis of polymer-based acid catalysts*

A typical procedure for preparing polymer-based acid catalyst was given as following. 1.5 g of 1-vinyl-3-(3-trimethoxysilylpropyl)-imidazolium chloride and 1.2 g of 1-vinyl-3-(3-sulfopropyl) imidazolium were introduced into a solution containing 25 ml of ethanol and 0.05 g of AIBN, followed by addition 1.2g of sodium p-styrene sulfonate. After stirring at room temperature for 3 h, the mixture was hydrothermally treated at 100 °C for 2 days in a 50 mL stainless steel autoclave reactor under nitrogen atmosphere. After evaporating the solvent at room temperature, the copolymer was hydrolyzed with TEOS (1.2 g, 5.6 mmol) in mixture medium of water and ethanol (volume ratio=1:10) at 60 °C for 24 h by using concentrated sulfuric acid as a catalyst. Finally, the resulting polymer catalysts were obtained by ion-exchange with 2 M sulfuric acid at room temperature, and washed thoroughly with water and alcohol,

dried at 60 °C in vacuum and designated as SO<sub>3</sub>H-PS-SO<sub>3</sub>H catalyst. Other polymer catalysts with the different molar ratio of monomers adopted under the synthetic condition have been prepared in a similar method (Table 1). The molar ratio of 1-vinyl-3-(3-sulfopropyl) imidazolium (3) to TEOS (4) was fixed at 1:1 in the all polymer catalysts.

### Characterization

All NMR spectra were recorded on a Bruker Avance III 400 instrument (400 MHz for <sup>1</sup>H) by using D<sub>2</sub>O as solvent. Chemical shifts (δ) are given in parts per million and coupling constants (J) in hertz. The elemental analysis of C, H, N was performed on an Elementar Vario EI III Elementa and ICP-AES analysis of S and Si on Vanan 710 instrument, respectively. FT-IR spectra were recorded at room temperature on a Niclet Fourier transform infrared spectrometer (Magna 550). Surface areas (BET) of the catalysts were measured by N<sub>2</sub> adsorption at 77 K using NOVA 4200e Analyser after the evacuation of the sample at 120 °C for 10 h. Thermogravimetric analysis(TGA) measurements were carried out by perkin Elmer Pyris Diamond in the current study and the constant heating rate of 10 °C/min was used in the air. Scanning electron microscopy (SEM) experiments were performed on JSM electron microscopes (JEOL JSM-6360LV, Japan). ICP-AES analysis was carried out on a Varian 710-ES instrument. The sample was pretreated with alkali fusion method prior to ICP-AES analysis. The acid loading of the sulfonic acid-functionalized polymer catalysts was determined by acid–base titration as the reported procedure.<sup>47</sup>

### Dehydration of sorbitol into 1,4-anhydro-D-sorbitol

The dehydration of sorbitol was performed in a 25mL Schlenk tube. 1.65 mmol of D-sorbitol, and 0.27 mmol of as-obtained catalyst were introduced into the reactor, and the tube was purged with nitrogen for three times. Then, the reactor was heated to 150 °C with vigorous stirring under nitrogen flow. After the reaction, the reactor was cooled to room temperature and water was added. The catalyst was filtrated to separate from the solution, and the catalyst was dried at 80 °C overnight and used for

the next run. The liquid products were analyzed using a HPLC (Agilent 1200 Series) equipped with a RI detector and a Shodex SUGAR SC1011 column (8 × 300 mm). The eluent was water with a flow rate of 1.0 cm<sup>3</sup> min<sup>-1</sup>. The column was thermostated at 80 °C by a column heater. The sampling loop has a volume of 10 μL. The conversion of sorbitol was calculated as follows: conversion (%) = 100 × (Moles of sorbitol reacted)/(Moles of sorbitol used in the reaction). Product selectivity of each product was calculated as follows: Product selectivity (%) = 100 × (Moles of carbon in a product defined)/(Moles of carbon in sorbitol reacted).

## Results and Discussion

### Catalyst preparation and characterization

The monomers 2 and 3 were prepared conveniently by the reported procedure.<sup>44,45</sup> Then the polymer was synthesized from solvothermal co-polymerization of 1, 2 and 3, followed by hydrolysis and condensation with 4 (TEOS). It was found that if only 1 and 2 were used for co-polymerization, the resulting copolymer was highly water-soluble and can not be separated after reaction. Thus in this work both of 3 and 4 have been necessarily used for producing polymer catalyst. The resulting polymer-based catalysts were obtained through ion-exchange of diluted H<sub>2</sub>SO<sub>4</sub> solution. The synthetic route for the SO<sub>3</sub>H-PS-SO<sub>3</sub>H polymer catalyst was shown in Scheme 2. All polymer catalysts with the different molar ratio of monomers were displayed in Table 1. It should be noted that all resulting polymer-based acid catalysts were subjected to elemental analysis and AES-ICP analysis, which proved that the polymerization can proceed effectively and almost all monomers were polymerized into polymer matrixes (Table 1S).

<Scheme 2>

<Table 1>

The polymer-based catalysts were firstly characterized by FT-IR spectra. Taking SO<sub>3</sub>H-PS-SO<sub>3</sub>H, SO<sub>3</sub>H-PS and PS-SO<sub>3</sub>H as examples, as shown in Figure 1, the FTIR spectra of catalysts (Fig. 1a, 1b and 1c) clearly showed the characteristic bands at 1185, 1126, 1038 cm<sup>-1</sup> that are attributed to -SO<sub>3</sub>H groups, which indicated that



Brønsted acidic sulfonic acid groups were deposited successfully on the polymer carbon framework. The bands ranged from 1400-1600  $\text{cm}^{-1}$  are attributed to the stretching vibrations of imidazole ring, indicating that imidazole ring structure has been embedded in the polymer matrix. The strong and broad peak at 3440  $\text{cm}^{-1}$  is assigned to the stretching vibration of -O-H in -SO<sub>3</sub>H groups and the shape is broad which indicated that there existed many intramolecular hydrogen bonds. The Si-O band stretching vibration can be also found at approximately 1009  $\text{cm}^{-1}$ . It was observed that the FT-IR spectra of PS-SO<sub>3</sub>H (Fig. 1a) and SO<sub>3</sub>H-PS (Fig. 1b) are almost the same with that of SO<sub>3</sub>H-PS-SO<sub>3</sub>H (Fig. 1c) except the stretching vibration of -O-H in -SO<sub>3</sub>H groups. It was observed that the -O-H stretching vibration of PS-SO<sub>3</sub>H and SO<sub>3</sub>H-PS was at 3451 and 3445  $\text{cm}^{-1}$ , respectively, while -O-H stretching vibration of SO<sub>3</sub>H-PS-SO<sub>3</sub>H was shifted to lower wavenumber (3440  $\text{cm}^{-1}$ ), compared with that of PS-SO<sub>3</sub>H and SO<sub>3</sub>H-PS, which might result from the effect of asymmetric hydrogen bonding interaction. Normally, lower vibration frequency of -O-H stretching vibration reflected stronger intramolecular hydrogen bonding interaction.<sup>48</sup> This implied that there might be stronger hydrogen bonding interaction among different type of sulfonic acid groups in four-component polymer catalyst (SO<sub>3</sub>H-PS-SO<sub>3</sub>H), in comparison with that of ternary polymer catalysts (PS-SO<sub>3</sub>H and SO<sub>3</sub>H-PS).

<Insert Fig. 1>

Fig. 1S showed the TGA curves of above three polymer-based catalysts. All samples gave three weight-loss steps: the first step below 200 °C is due to the desorption of water; the second step between 250 and 400 °C is attributed to the decomposition of sulfate species on the samples; the third step between 450 and 580 °C is attributed to the destruction of polymer framework, respectively.<sup>49</sup> Based on the TG analysis, the residual silica species are estimated as 10.68 wt%, 6.28 wt% and 11.95 wt% (Fig. 1S, A, B and C), respectively which is well consistent with the results of ICP (Table 1S, entries 1, 7 and 9). In addition, it was demonstrated from TGA curves that four-component SO<sub>3</sub>H-PS-SO<sub>3</sub>H catalyst showed higher thermal stability, in comparison with the ternary SO<sub>3</sub>H-PS and PS-SO<sub>3</sub>H catalysts.

Furthermore, as observed in Table 2S, conventional acid macroporous resin Amberlyst 15 had high content of sulfonic groups ( $4.7 \text{ mmol}\cdot\text{g}^{-1}$ ) and about  $45 \text{ m}^2/\text{g}$  of surface area, while the polymer-based catalysts exhibited slightly lower BET surface area than that of Amberlyst 15. Fig. 2S shows the  $\text{N}_2$  isotherms of  $\text{SO}_3\text{H-PS-SO}_3\text{H}$ ,  $\text{SO}_3\text{H-PS}$  and  $\text{PS-SO}_3\text{H}$ . All of the samples showed type-IV isotherms but no sharp capillary condensation step, indicating low porous properties. In addition, as shown in Table 1, the acidity of different polymer catalysts can be adjusted, and the polymer acidity was tuned from  $0.48 \text{ mmol}\cdot\text{g}^{-1}$  to  $3.25 \text{ mmol}\cdot\text{g}^{-1}$  (Table 1, entries 1, 3, 5, 7 and 9), but still lower than that of Amberlyst 15 ( $4.7 \text{ mmol}\cdot\text{g}^{-1}$ , Table 1, entry 17).

### Catalytic performance

Firstly, the catalytic evaluation of the dehydration of sorbitol was carried out in the flow of nitrogen under water-free conditions by using various acid catalysts. As shown in Table 2, it can be observed that sorbitol was hard to be converted in the absence of any catalyst (Table 2, entry 1). Even if the reaction temperature was raised to  $180 \text{ }^\circ\text{C}$  without a catalyst, the conversion of sorbitol was only 7.5% after 10 h (not shown). Conventional solid acid catalysts like Amberlyst-15 and HZSM-5 are catalytically active for this reaction, giving 100% and 82.3% of sorbitol conversion at  $150 \text{ }^\circ\text{C}$  for 4 h, respectively, and the main dehydration products were isosorbide with 62.3 and 52.5% of selectivities, respectively (Table 2, entries 2 and 3). In addition, it was found that the liquid acid catalysts such as  $\text{H}_2\text{SO}_4$  and sulfonic acid group functionalized ionic liquid (IL- $\text{HSO}_4$ ) gave similar conversion of sorbitol and the selectivity toward isosorbide as that of solid acid catalysts above (Table 2, entries 4 and 5). Interestingly, the present polymer catalysts can produce 1,4-anhydro-D-sorbitol directly from sorbitol under solvent free and relatively mild conditions. It was worth noting that although  $\text{PS-SO}_3\text{H}$ ,  $\text{SO}_3\text{H-PS}$  and  $\text{SO}_3\text{H-PS-SO}_3\text{H}$  polymer catalysts afforded lower TOF values, compared with these of the conventional solid acid catalysts (Table 2, entries 2 and 3) and the homogeneous catalysts (Table 2, entries 4 and 5), they indeed exhibited excellent

selectivity to 1,4-anhydro-D-sorbitol (Table 2, entries 6-8).

<Insert Table 2>

In the next step, the effect of acidity of the polymer-based catalysts on the catalytic performance of sorbitol dehydration is shown in Fig. 2. The sorbitol conversion was increased from 30.2% to 100%, while selectivity toward 1,4-anhydro-D-sorbitol decreased from 90.2% to 22.3%, and meanwhile the selectivity of isosorbide was increased from 0 to 65.4% accordingly as the acidity enhanced from  $0.48 \text{ mmol}\cdot\text{g}^{-1}$  to  $4.86 \text{ mmol}\cdot\text{g}^{-1}$ . This demonstrated that an appropriate acidity was very crucial for the selective dehydration of sorbitol to 1,4-anhydro-D-sorbitol. It can be observed that  $1.82 \text{ mmol}\cdot\text{g}^{-1}$  of acidity (corresponding to  $\text{SO}_3\text{H-PS-SO}_3\text{H}$  catalyst) should be mostly appropriate for selective dehydration of sorbitol into 1,4-anhydro-D-sorbitol.

<Insert Figure 2>

The  $\text{SO}_3\text{H-PS-SO}_3\text{H}$  catalyst was found to be highly hydrophilic, which can be confirmed by water contact angle measurements. As shown in Fig. 3S, the water contact angle of  $\text{SO}_3\text{H-PS-SO}_3\text{H}$  was about  $10^\circ$ . Highly hydrophilic catalyst surface might keep primary dehydration product 1,4-anhydro-D-sorbitol off the catalyst surface due to strong water adsorption, preventing the reaction to move to the second dehydration step. As shown in Scheme 3, sorbitol can be dehydrated into 1,4-anhydro-D-sorbitol with  $\text{SO}_3\text{H-PS-SO}_3\text{H}$ , because of the hydrophilic surface, water produced in the reaction could cover the surface of the catalyst, preventing 1,4-anhydro-D-sorbitol further to dehydrate into more hydrophobic isosorbide. Thus the particular catalytic performance of the present polymer acid catalysts should be directly attributed to the appropriate acidity and hydrophilic surface.

<Insert Scheme 3>

The effect of reaction temperature on the sorbitol conversion has been shown in Fig. 3A. The sorbitol conversion over  $\text{SO}_3\text{H-PS-SO}_3\text{H}$  catalyst was increased from 31.8% to 93.4% and the selectivity to 1,4-anhydro-D-sorbitol always retained more than 90% accordingly, as the reaction temperature increased from  $120^\circ\text{C}$  to  $150^\circ\text{C}$ . However, sorbitol conversion only increased slightly and the selectivity to

1,4-anhydro-D-sorbitol decreased gradually as reaction temperature was further increased up to 170 °C. It was observed that the product 1,4-anhydro-D-sorbitol was further transformed into isosorbide and other by-products under higher temperature. This demonstrated that an appropriate reaction temperature was crucial for the conversion of sorbitol to 1,4-anhydro-D-sorbitol. As a result, the optimal temperature for producing 1,4-anhydro-D-sorbitol was around 150 °C.

The influence of reaction time on the conversion of sorbitol was also examined. As shown in Fig. 3B, almost complete conversion of sorbitol was achieved after 4h and the selectivity to 1,4-anhydro-D-sorbitol kept at more than 95%. However, the sorbitol conversion remained about the same though prolong the reaction time to 7h, which indicated that the present catalyst can catalyze the dehydration of sorbitol to 1,4-anhydro-D-sorbitol with high efficiency. The selective dehydration of sorbitol to 1,4-anhydro-D-sorbitol was also dependent on the catalyst dosage. As shown in Fig. 4C, the sorbitol conversion was 40.5% when only 0.11 mmol acid amount (0.06 g  $\text{SO}_3\text{H-PS-SO}_3\text{H}$ ) was used. Nevertheless, the sorbitol conversion increased up to over 98% sharply with an increasing acid amounts to 0.27 mmol and then no further increase in sorbitol conversion were observed with further increasing in catalyst dosage. It should be worth noting that the selectivity to 1,4-anhydro-D-sorbitol always kept at more than 95% when the sorbitol dehydration reaction was performed under mild conditions (Fig. 3B and 3C)

<Insert Figure 3>

Sequentially, the reaction network of sorbitol dehydration on  $\text{SO}_3\text{H-PS-SO}_3\text{H}$  was investigated by means of kinetic analysis (Scheme 1), where the symbols  $K_1$ - $K_3$  represented reaction rate constants. The constant  $K_1$  describes the 1,4-cyclodehydration of sorbitol to 1,4-anhydro-D-sorbitol, and the constant  $K_2$  describes the 1,4-cyclodehydration of 1,4-anhydro-D-sorbitol to isosorbide. The constant  $K_3$  describes other dehydration and degradation pathways of sorbitol to by-products. As the main products was 1,4-anhydro-D-sorbitol, the pathways for the other products can be represented by a single constant,  $K_3$ . Moreover, logarithmic changes of concentrations of sorbitol or 1,4-anhydro-D-sorbitol with time were

approximately linear therefore, these reactions could be considered to occur as consecutive irreversible first-order reactions. The corresponding reaction estimated from Arrhenius equation fits using the rate constants at the respective temperatures. Fig. 4S showed dependences of catalytic activities on reaction time at the beginning of sorbitol dehydration at the temperature of 120-150 °C over SO<sub>3</sub>H-P-SO<sub>3</sub>H catalyst. After fitting, apparent activation energies ( $E_a$ ) have been estimated, as presented in Figure 5. Notably, the apparent activation energy of SO<sub>3</sub>H-P-SO<sub>3</sub>H is 63.57 kJ/mol, which was slightly lower than that reported previously.<sup>42</sup>

<Insert Figure 4>

We nextly examined the recyclability of SO<sub>3</sub>H-PS-SO<sub>3</sub>H catalyst. As shown in Fig. 5, the catalyst can be reused five times with only a slight decrease in activity but the selectivity to 1,4-anhydro-D-sorbitol kept very high and unchanged during in the consecutive recycles. As shown in Table 1, the spent the four-component catalysts showed nearly no obvious decrease in acidity as compared with that of the fresh ones (Table 1, entry 1-10). For example, after five consecutive recycles, the amount of acid sites of SO<sub>3</sub>H-PS-SO<sub>3</sub>H catalyst was determined by the titration method and found to be 1.75 mmol•g<sup>-1</sup>, which was only slightly lower that of the fresh catalyst (1.82 mmol•g<sup>-1</sup>), indicating that the SO<sub>3</sub>H-PS-SO<sub>3</sub>H was highly acid leaching-resistant. In contrast, either PS-SO<sub>3</sub>H or SO<sub>3</sub>H-PS catalyst showed very poor recyclability in sorbitol dehydration reaction (Fig. 5S, A and B). Both of the spent ternary PS-SO<sub>3</sub>H and SO<sub>3</sub>H-PS catalysts showed obvious loss in acidity and sulfur content, as compared with those of the fresh one (Table 1, entries 11 vs 12, 13 vs 14; Table 1S, entries 7 vs 8, 9 vs 10). All these results suggested that the leaching of acid was most likely the main reason for catalyst deactivation. This implied that there might be synergistic effect between alkyl sulfonic acid groups and aryl sulfonic acid groups over the four-component SO<sub>3</sub>H-PS-SO<sub>3</sub>H catalyst, as compared with that over ternary PS-SO<sub>3</sub>H or SO<sub>3</sub>H-PS catalyst. As proved above by FT-IR (Fig. 1), there is stronger intramolecular hydrogen bonding over the four-component SO<sub>3</sub>H-PS-SO<sub>3</sub>H catalyst (Scheme 3), which played an important role in inhibiting acid leaching. Actually, the effect of specific hydrogen bonding interaction between adjacent acid pairs on the

acid catalysis has attracted great interests recently.<sup>[50,51]</sup>

The thermal stability of the catalyst was also high and the sulfate groups were intact at reaction temperature, as demonstrated by the TG data in Fig. 1S(A, B and C). In addition, as displayed in Fig. 1, the characteristic peaks arisen from sulfuric acid remain unchanged after five runs. Thus, it can be concluded that the SO<sub>3</sub>H-PS-SO<sub>3</sub>H catalyst can be easily recycled without any noticeable loss of catalytic performance.

Fig. 6 showed the scanning electron microscopy (SEM) images of the fresh SO<sub>3</sub>H-P-SO<sub>3</sub>H and the spent SO<sub>3</sub>H-PS-SO<sub>3</sub>H catalysts. Both of catalysts showed rough surfaces and abundant sponge-like bulk pores. No significant difference in SEM images can be observed, although the spent SO<sub>3</sub>H-PS-SO<sub>3</sub>H catalyst seemed to show more fine particles than the fresh one.

<Insert Figure 6>

## Conclusions

In summary, we have demonstrated that solvent-free dehydration of sorbitol for the preparation of 1,4-anhydro-D-sorbitol is effective. Catalytic tests have shown that the present polymer catalysts exhibit extraordinary catalytic activities and selectivity to 1,4-anhydro-D-sorbitol, which mainly attributes to its appropriate acidity and hydrophilicity. In addition, it has been indicated that the quaternary SO<sub>3</sub>H-PS-SO<sub>3</sub>H catalysts containing two-type of Brønsted acid site are more efficient and robust for 1,4-anhydro-D-sorbitol production than that containing a single Brønsted acid site (PS-SO<sub>3</sub>H and SO<sub>3</sub>H-PS) used in this work. It is believed that hydrogen bonding interaction played a crucial role in improving recyclability of polymer-based acid catalysts. The polymer-based acid catalysts showed the huge advantage of tunable acidity, easy preparation, excellent catalytic activity and selectivity to 1,4-anhydro-D-sorbitol and thus open new avenues for preparation of efficient solid acid for the transformation of biomass into value-added chemicals.

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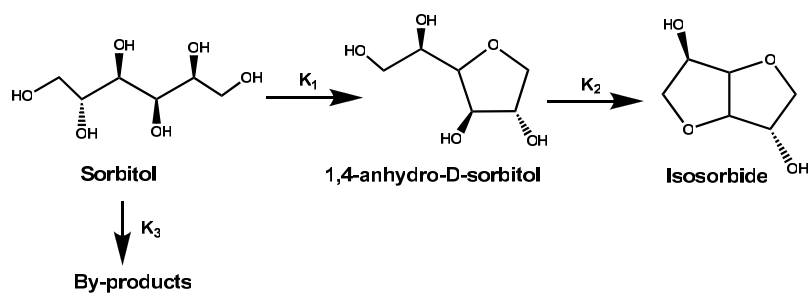
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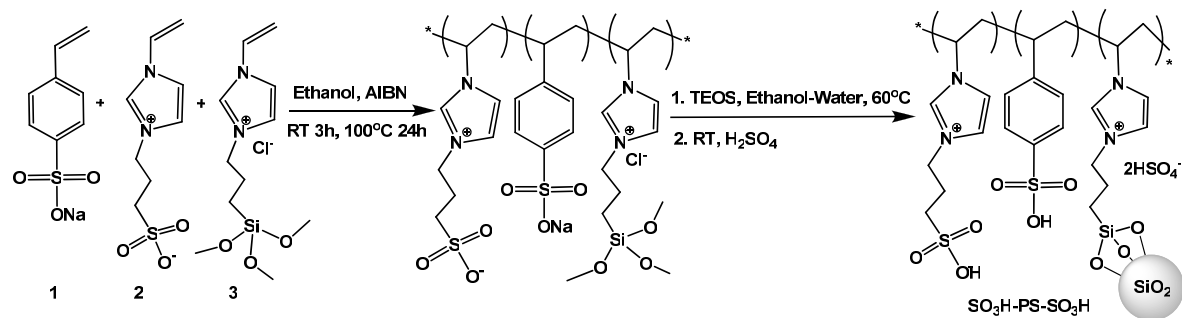


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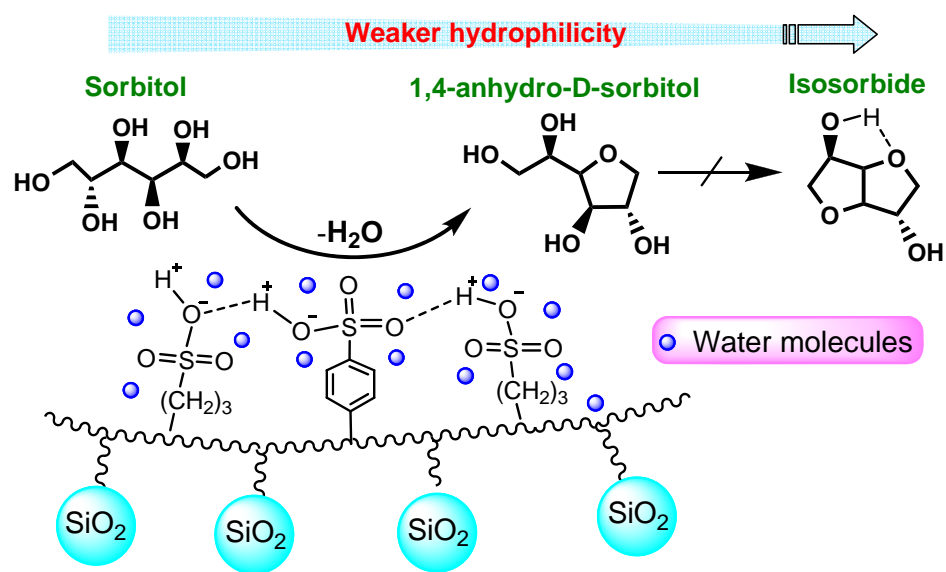
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Scheme 1. Reaction pathway of sorbitol dehydration.



Scheme 2. Synthetic route for the polymer-based catalyst



Scheme 3. The process for the sorbitol dehydration into 1,4-anhydro-D-sorbitol.

Table 1 The various polymer-based acid catalysts

Entry	Catalysts	Molar ratio of 1:2:3:4 <sup>a</sup>	Acidity <sup>b</sup> (mmol•g <sup>-1</sup> )
1	SO <sub>3</sub> H-PS-SO <sub>3</sub> H	1:1:1:1	1.82
2 <sup>c</sup>	SO <sub>3</sub> H-PS-SO <sub>3</sub> H		1.75
3	0.3SO <sub>3</sub> H-PS-0.3SO <sub>3</sub> H	0.3:0.3:1:1	0.48
4 <sup>c</sup>	0.3SO <sub>3</sub> H-PS-0.3SO <sub>3</sub> H		0.40
5	0.6SO <sub>3</sub> H-PS-0.6SO <sub>3</sub> H	0.6:0.6:1:1	1.06
6 <sup>c</sup>	0.6SO <sub>3</sub> H-PS-0.6SO <sub>3</sub> H		0.99
7	2SO <sub>3</sub> H-PS-2SO <sub>3</sub> H	2:2:1:1	2.30
8 <sup>c</sup>	2SO <sub>3</sub> H-PS-2SO <sub>3</sub> H		2.20
9	3SO <sub>3</sub> H-PS-3SO <sub>3</sub> H	3:3:1:1	3.25
10 <sup>c</sup>	3SO <sub>3</sub> H-PS-3SO <sub>3</sub> H		3.16
11	SO <sub>3</sub> H-PS	1:0:1:1	1.78
12 <sup>c</sup>	SO <sub>3</sub> H-PS		1.12
13	PS-SO <sub>3</sub> H	0:1:1:1	1.73
14 <sup>c</sup>	PS-SO <sub>3</sub> H		1.08
15	H <sub>2</sub> SO <sub>4</sub>	-	20
16	Amberlyst 15	-	4.70
17	HZSM-5	-	2.62

<sup>a</sup> Represented the molar ratio of different monomers, <sup>b</sup> Obtained by acid–base titration,

<sup>c</sup> The catalyst was recycled for five times in sorbitol dehydration.

Table 2 Dehydration of sorbitol over various acid catalysts<sup>a</sup>

Entry	Catalyst	Sorbitol Conv. (%)	Product Sel. (%)		TOF/h <sup>b</sup>
			1,4-anhydro-D-sorbitol	Isosorbide	
1	-	3.5	-	-	
2	Amberlyst-15	>99	10.8	62.3	14.4
3	HZSM-5	82.3	23.4	52.5	7.0
4	H <sub>2</sub> SO <sub>4</sub>	>99	15.3	76.3	19.2
5	IL-HSO <sub>4</sub>	>99	25.2	65.4	7.9
6	PS-SO <sub>3</sub> H	85.1	82.3	-	3.5
7	SO <sub>3</sub> H-PS	88.6	85.4	-	3.8
8	SO <sub>3</sub> H-PS-SO <sub>3</sub> H	94.3	93.4	-	4.1

<sup>a</sup> Reaction conditions: 150 °C, 4h, Sorbitol (1.65 mmol), Catalyst (Acid amounts: 0.27 mmol), N<sub>2</sub> flow. <sup>b</sup> The TOF was defined as moles of sorbitol converted per mole acid site per hour with the conversion lower than 15%.

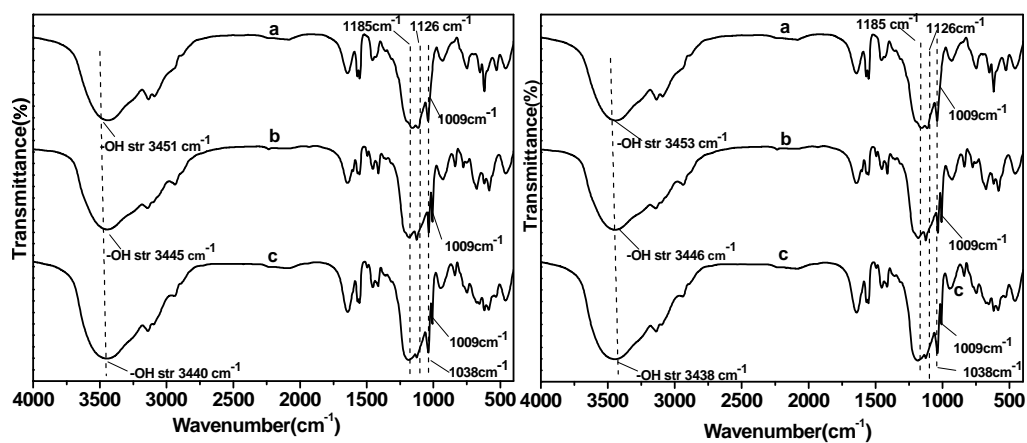


Fig. 1. FTIR spectra of fresh catalysts (left) and the spent catalysts (right) after the fifth times. a) PS-SO<sub>3</sub>H, b) SO<sub>3</sub>H-PS and c) SO<sub>3</sub>H-PS-SO<sub>3</sub>H.



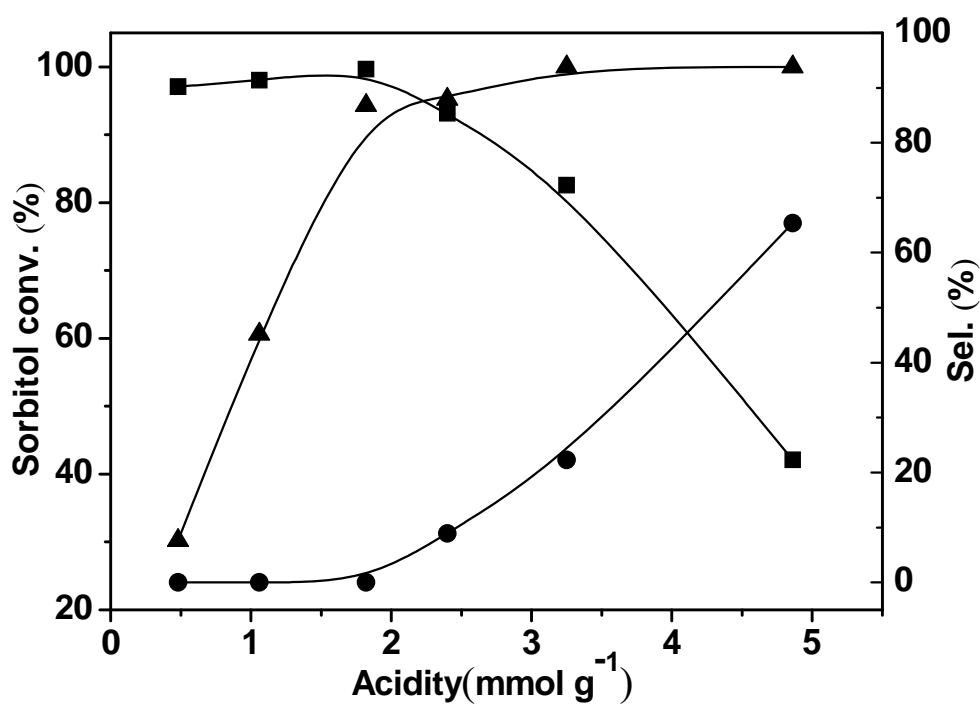


Fig. 2. Effect of acidity of the polymer catalysts on the performance of sorbitol dehydration. Reaction conditions: 150 °C, 4h, 1.65mmol sorbitol; Catalysts(acid amounts: 0.27 mmol), (▲) Sorbitol conversion, (■) Selectivity to 1,4-anhydro-D-sorbitol, (●) Selectivity to isosorbide.

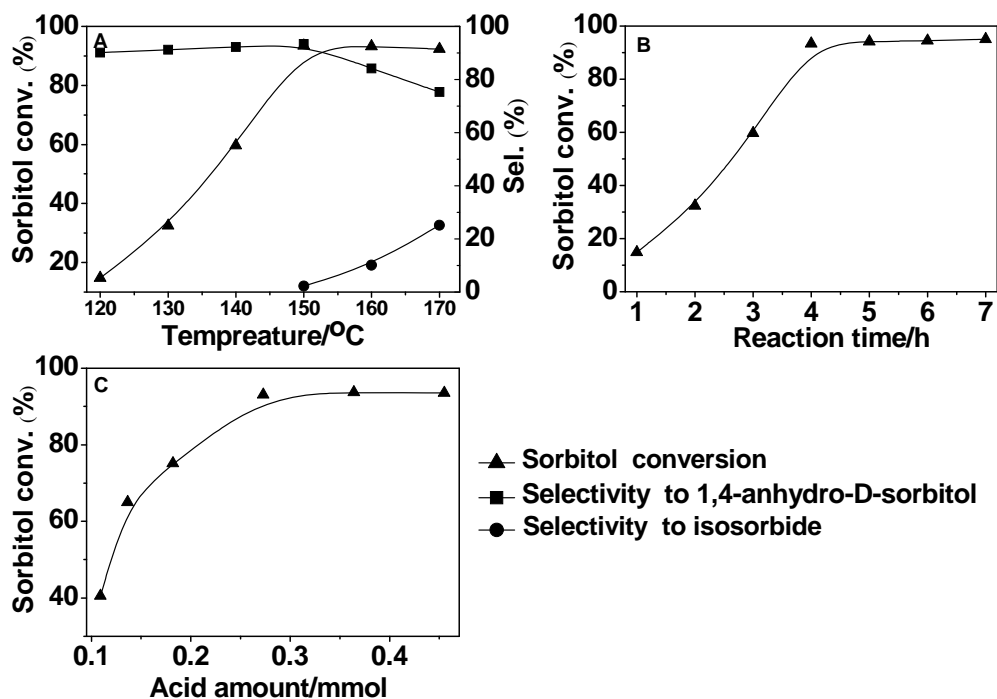


Fig. 3 A) Effect of reaction temperature on the sorbitol dehydration after reaction for 4 h. B) Time profile of sorbitol dehydration at 150°C. C) Effect of acid amount on the sorbitol conversion at 150 °C for 4 h [Acid amount (mmol)=catalyst mass (g)×1.82 mmol•g<sup>-1</sup>]. The selectivity to 1,4-anhydro-D-sorbitol are always than 95% in Fig.3 B and 4C. Reaction conditions: Sorbitol (1.65 mmol) for A, B and C, SO<sub>3</sub>H-PS-SO<sub>3</sub>H catalyst (acid amounts: 0.27 mmol) for A and B.

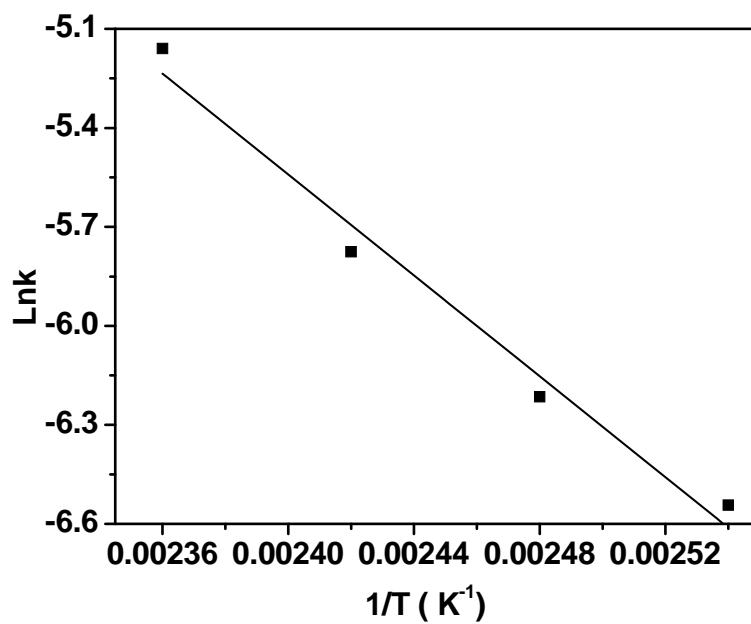


Fig. 4 Experimental points correlating the inverse of the absolute temperature ( $1/T$ ) with the initial reaction rates ( $\ln k$ ) over  $\text{SO}_3\text{H-PS-SO}_3\text{H}$  catalyst. The straight lines are made with the best fitting of the experimental points.

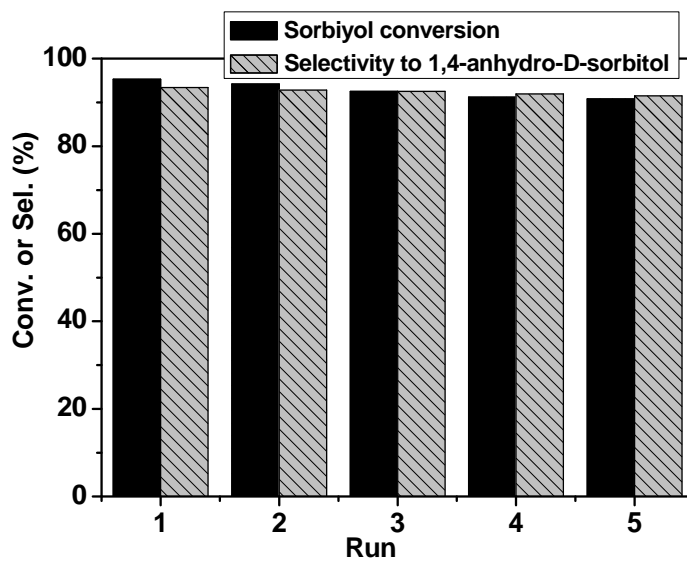


Fig. 5 Recyclability of the  $\text{SO}_3\text{H-PS-SO}_3\text{H}$  catalyst in sorbitol dehydration. Reaction condition:  $150\text{ }^\circ\text{C}$ , 4h, sorbitol: 1.65 mmol and catalyst(acid amounts: 0.27 mmol).

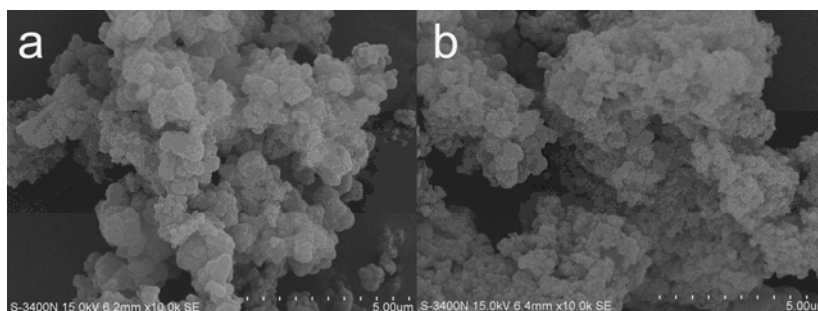


Fig. 6 SEM images of (a) fresh  $\text{SO}_3\text{H-P-SO}_3\text{H}$ , (b)  $\text{SO}_3\text{H-P-SO}_3\text{H}$  after the fifth catalytic cycles.