

Solvent-Free Production of Isosorbide from Sorbitol Catalyzed by a Polymeric Solid Acid

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A series of polymeric solid acid catalysts (PDSF-x) is prepared by grafting strong electron-withdrawing groups ($-SO_2CF_3$) on a sulfonic acid-modified polydivinylbenzene (PDS) precursor synthesized hydrothermally. The effect of acid strength on sorbitol dehydration is investigated. The textural properties, acidity, and hydrophobicity are characterized by using Brunauer– Emmett–Teller analysis, elemental analysis, and contact angle tests. The results of FTIR spectroscopy and X-ray photoelectron spectroscopy show that both $-SO_3H$ and $-SO_2CF_3$ are grafted onto the polymer network. We used solid-state ³¹P NMR spec-

Introduction

Biomass resources, as an abundant renewable carbon resource in nature, are considered as a promising alternative to non-renewable fossil fuels in the production of value-added chemical products and fuels.^[1] Sorbitol, a "top 10" valued-added biobased building block, is obtained from cellulose by the hydrogenation of glucose.^[2] Since the 1940s,^[3] the use of sorbitol as a feedstock in biorefinery has attracted much attention. Isosorbide, the doubly dehydrated product of p-sorbitol, and its derivatives have been used widely in the fields of medicine,^[4] food, cosmetics,^[5] and polymers.^[6]

For the sorbitol dehydration reaction, a mechanism accepted widely is the intramolecular $S_N 2$ substitution reaction.^[7] For example, isosorbide is produced by the formation of 1,4-sorbitan (or 3,6-sorbitan) followed by dehydration. The second step requires a higher reaction temperature and a longer reaction time than the first step under the same conditions.^[7,8] However, as a result of the effects of chemo- and regioselectivity, byproducts such as isomers and humins are likely to be formed during the double dehydration reaction.^[9] Therefore,

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troscopy to show that the acid strength of PDSF-*x* is enhanced significantly compared with that of PDS, especially for PDSF-0.05. As a result, PDSF-0.05 exhibits the highest isosorbide yield up to 80%, a good turnover frequency of 231.5 h⁻¹ (compared to other catalysts), and excellent cyclic stability, which is attributed to its large specific surface area, appropriate acid strength, hydrophobicity, and stable framework structure. In addition, a plausible reaction pathway and kinetic analysis are proposed.

the key to the production of isosorbide is a suitable acid catalyst to promote the complete conversion and a high selectivity to sorbitol.

Homo- and heterogeneous catalysts have been used in the sorbitol dehydration reaction. Traditional homogeneous catalysts, such as mineral acids (H₂SO₄, HCl, H₃PO₄, etc.),^[10] Lewis acids,^[10b,11] and ionic liquids,^[12] favor isosorbide formation. However, corrosion, environmental harm, and poor reusability limit their industrial applications. Consequently, the development of an economic and environmentally friendly solid catalyst is critical to obtain a high yield of isosorbide. To date, different heterogeneous catalysts, such as acid resins,^[13] zeolites,^[14] metal phosphates,^[15] supported metal oxides,^[16] sulfated and phosphate metal oxides,^[17] supported heteropolyacids,^[18] and carbon-based acids,^[19] have been employed for the sorbitol dehydration reaction. Generally, the catalytic activity of solid acid catalysts is worse than that of homogeneous acids.^[20] An important reason for this is that the acid sites on the solid acid catalyst cannot generate cooperative effects as in homogeneous catalysts.^[21] Therefore, the design of efficient sorbitol-dehydration catalysts, such as the regulation of acid sites, acid strength, thermal stability, and hydrophilic/hydrophobic properties, still poses many challenges.

In this sense, sulfonate resins have been evaluated as solid acid catalysts for sorbitol dehydration. Goodwin et al. studied sorbitol dehydration over Amberlite IR-120 type resin, over which an isosorbide yield of 39% was obtained.^[22] Bock et al. found that the isosorbide yield reached 57% under harsh reaction conditions (170 °C, 2 h, 10 mmHg) over the same catalyst.^[8] Since then, resin-type solid acid catalysts have gained considerable attention because of their large specific surface area, controllable acidity, and hydrophobicity. Commercial ion-



exchange resins such as Amberlyst, Purlite, and Nafion have been used.^[13c,d,h] Although some commercial ion-exchange resins are able to achieve a good sorbitol yield (>70%), their thermal stability needed to be improved. The SA-SiO₂-x catalysts synthesized by Shi et al. were able to achieve an isosorbide yield of 84% under mild reaction conditions.^[13g] Despite the good performance of propylsulfonic acid functionalized SBA-15, the stability of the catalyst was poor.^[13e] Zhang et al. found that hydrophobic P–SO₃H can catalyze the dehydration efficiently, and 87.9% isosorbide yield was obtained.^[13b] Previously, we found that the polymer network and acidity of sulfonic acid-modified polydivinylbenzene (PDS) solid acid catalysts have an important effect on the dehydration reaction of sorbitol, and a yield of 81.7% can be obtained.^[13a]

Dabbawala et al. found that Brønsted acids can catalyze the dehydration of sorbitol efficiently and that the acid strength has a significant effect on the reaction.^[10a] Recently, Cubo et al. claimed that although the increased acid strength limited the first step to some extent, the second step could be accelerated effectively.^[13e] In addition, the hydrophobicity of the catalyst surface also has a crucial effect on sorbitol dehydration, that is, the hydrophobic surface is able to remove the water produced by the reaction from the surface rapidly, which prevents the coverage of the acid sites with water and leads to decreased activity.^[13a,b, 14a,b, 23] According to previous reports and our research, the acid strength of the catalyst plays an important role to improve the sorbitol conversion and the selective transformation to isosorbide. However, there is no systematic study on the influence of the acid strength of solid acid catalysts on sorbitol conversion.

In this study, a series of heterogeneous acid catalysts (PDSF-x, polydivinylbenzene solid acid catalyst modified by sulfonic acid group and trifluoromethanesulfonic acid group) with different acid strengths was prepared by grafting different amounts of strongly electron-withdrawing trifluoromethanesulfonic acid groups (-SO₂CF₃). The textural properties, morphologies, acid properties, coordination environment, and thermal stability of the samples were studied. The acid sites that are actually exposed to the reactants play a crucial role in the catalytic effect of the sorbitol dehydration reaction. The relationship between the properties and the catalytic performance of the catalysts was discussed. The results showed that a sorbitol conversion of 100% and isosorbide yield of 80% can be obtained at 140°C without solvent.

Results and Discussion

The preparation of SO_2CF_3 -modified polydivinylbenzene solid acid catalyst (PDVBF), PDS, and PDSF-*x* is shown in Scheme S1. The PDSF-*x* catalysts were synthesized in three steps. Firstly, the precursor PDSNa (divinylbenzene and sodium p-styrene sulfonate polymer) was synthesized. Then, the dried white solid was ion-exchanged in 1 \bowtie H₂SO₄ solution for 24 h to obtain the PDS catalyst. Finally, the $-SO_2CF_3$ group was grafted onto the PDS catalyst by acidification with CF_3SO_3H .

Characterization

N₂ adsorption-desorption isotherms and pore size distribution curves of all samples are presented in Figure 1, and the textural information is summarized in Table 1. A type-IV isotherm with an H4 hysteresis loop at a high relative pressure confirms the presence of mesopores.^[24] The precursor (PDVB) has large specific surface area (1008 m²g⁻¹) and pore volume $(1.88 \text{ cm}^3 \text{g}^{-1})$ and an average pore diameter (9.14 nm; Table 1), which favor the grafting of acid groups. If -SO₃H and -SO₂CF₃ groups were grafted alone, the specific surface area of the catalysts decreased slightly (Table 1, Entries 2 and 3). However, as the grafting amount of -SO₂CF₃ increased, the specific surface area, pore volume, and pore diameter of the catalysts decreased gradually (Table 1, Entries 3-8) as a result of the grafting of acid groups on the inner and outer surfaces of the catalysts, which is consistent with our previous work.^[13a] The decrease in the specific surface area of PDSF-x samples may be attributed to the acid groups that occupy the surface of the polymer network that cannot contribute to the specific surface area.^[25] In addition, the grafted acid groups may block the pores and cause a decrease in the pore size and pore volume in accordance with the results of Liu et al.^[26]

The elemental analysis and acid–base titration results for all of the catalysts are summarized in Table 1. Compared with that of PDS (0.3) (1.38 mmol g⁻¹), the S content increased gradually upon the grafting of $-SO_2CF_3$ groups (1.37–3.73 mmol g⁻¹). In-



Figure 1. $N_{\rm 2}$ adsorption–desorption isotherms (left) and pore size distribution curves (right) of the catalysts.



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Entry	Catalyst	S content $[mmol g^{-1}]^{[a]}$	Acid exchange capacity $[mmol g^{-1}]^{[b]}$	$S_{BET} [m^2 g^{-1}]^{[c]}$	$V_{\rm p} [{\rm cm}^3 {\rm g}^{-1}]^{[{\rm d}]}$	D _p [nm] ^[e]
1	PDVB	0.00	0.00	1008	1.88	9.14
2	PDS(0.3)	1.38	1.53	715	1.52	9.49
3	PDVBF-0.05	0.29	0.25	806	1.74	9.61
4	PDSF-0.01	1.37	1.43	658	1.16	8.02
5	PDSF-0.05	1.75	1.12	485	0.63	6.08
6	PDSF-0.1	1.97	1.01	323	0.30	4.30
7	PDSF-0.15	2.34	1.03	247	0.25	4.93
8	PDSF-0.2	3.73	1.17	243	0.27	5.46
9	PDSF-0.05 ^[f]	1.52	1.08	427	0.49	5.24

terestingly, the total S content of PDS (0.3) (1.38 mmolg⁻¹) and PDVBF-0.05 (0.29 mmolg⁻¹) was approximately equal to that of PDSF-0.05 (1.75 mmolg⁻¹), which indicates that both acid groups ($-SO_3H$ and $-SO_2CF_3$) were grafted successfully onto the catalysts. However, according to the results of acid-base titration, as the grafting amount of the $-SO_2CF_3$ group increases, the amount of accessible H⁺ sites of the catalyst sample was somehow lower than the S content obtained by elemental analysis. This phenomenon is probably caused by the poor swelling ability of the resin particles in the reaction system,^[27] and Zhang et al. obtained similar results.^[21]

Powder XRD patterns of all catalysts are shown in Figure S1. All samples showed broad Bragg reflection peaks at approximately $2\theta = 15-25^{\circ}$ attributed to the amorphous structure of the catalysts. The overall structure of the catalysts did not change significantly before and after the grafting of $-SO_2CF_3$.

The morphologies of PDVB, PDS (0.3), and PDSF-0.05 were examined by using SEM and TEM (Figure S2). The polymer matrix of PDVB shows an irregular coralline villus structure (Figure S2 a), whereas PDS (0.3) grafted with $-SO_3H$ has a loose spongy structure (Figure S2 b). Notably, the fluffy structure of the catalyst disappeared after the grafting of $-SO_2CF_3$ (Figure S2 c) to form a rough surface composed of many small particles. According to the TEM images (Figure S2 d–f), the catalysts have an abundant wormhole-like mesoporous structure (5–50 nm) after the grafting of acid groups. Compared with that in the TEM image of PDS (0.3), the black portion of PDSF-0.05 increased, which suggests that $-SO_2CF_3$ is grafted successfully into the pores.

Water droplet contact angles of the catalyst are presented in Figure S3. The hydrophobic angles of PDVB, PDS (0.3), and PDSF-0.05 are 153, 147, and 140°, respectively (Figure S3 a–c). However, if the grafting amount of $-SO_2CF_3$ was increased (x > 0.05), the catalysts lost their hydrophobic properties. This may be because excessive super acid (CF₃SO₃H) destroys the surface structure of the catalysts, which is consistent with the results obtained by using SEM.

Adsorption isotherms of water on PDVB, PDS (0.3), PDVBF-0.05, PDSF-0.05, and Amberlyst-15 are shown in Figure S4. Notably, all synthesized catalysts exhibit a much lower water absorption capacity than Amberlyst-15. The water absorption of PDS (0.3) is larger than that of PDSF-0.05, probably because of its larger specific surface area (715 vs. 485 $m^2 g^{-1}$). These results are consistent with those of the water droplet contact angles.

FTIR spectra of all samples are shown in Figure S5. The band located at $\tilde{\nu} = 1030-1040 \text{ cm}^{-1}$ is associated with the C–S stretch on the benzene rings. Characteristic absorptions of – SO₃H at $\tilde{\nu} = 1008$, 1125, and 1178 cm⁻¹ are caused by the symmetrical and asymmetrical stretching vibrations of O=S=O.^[28] In addition, for the PDSF-*x* catalysts, the absorption of C–F appeared at $\tilde{\nu} = 1290 \text{ cm}^{-1}$, the intensity of which increased gradually with the increase of the amount of grafted $-SO_2CF_3$.^[29] These results suggest that $-SO_3H$ and $-SO_2CF_3$ are grafted on the PDVB, which is in accordance with the results obtained by using elemental analysis.

X-ray photoelectron spectra (XPS) of PDS (0.3), PDVBF-0.05, and PDSF-0.05 are presented in Figure 2. The spectra of all samples show characteristic peaks of C, S, and O elements (Figure 2a). Peaks with binding energies (BE) of approximately 533 and 285 eV are attributed to C1s and O1s. In addition, a new peak of F1s (ca. BE=690 eV) appeared in the spectra of PDVBF-0.05 and PDSF-0.05 (Figure 2a-c). Notably, the S2p peak in the spectra of PDS (0.3) and PDVBF-0.05 appears at BE = 164.3 and 169.1 eV, respectively, whereas that of PDSF-0.05 appears at BE = 168.8 eV (Figure 2b). This might be because of the introduction of the strong electron-withdrawing group -SO₂CF₃, which enhances the acid strength of the catalysts.^[30] This conclusion is consistent with the results obtained by using EPR spectroscopy (Figure S6). Peaks of C-C (BE = 284.7 eV), C–S (BE = 286.2 eV), and C–F (BE = 291.4 eV) are observed in the C1s high-resolution XPS spectrum of PDSF-0.05 (Figure 2 c), which indicate that the $-SO_2CF_3$ group was grafted onto PDS (0.3).^[29]

According to previous reports, the introduction of F increases the acid strength and thermal stability of Nafion.^[31] To gain a deep structural insight into the samples, ³¹P magic-angle spinning (MAS) NMR spectra of the probe trimethylphosphine oxide (TMPO) adsorbed on PDS (0.3), PDVBF-0.05, and PDSF-*x* were collected (Figure 3). This method can be used to identify multiple acid sites on the catalyst efficiently according to the strength of the interaction between TMPO and a Brønsted acid. The relationship between proton affinity (PA) and $\delta^{^{31}P}$ is $\delta^{^{31}P} = 182.866 - 0.3902*PA$, and a PA value of 250 kcal mol⁻¹ (85.3 ppm) is the threshold for superacidity.^[32] Therefore, the



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Figure 2. a) Survey, b) S 2p, and c) C 1s XPS spectra of PDS (0.3), DVBF-0.05, and PDSF-0.05.



Figure 3. ³¹P MAS NMR spectra of TMPO adsorbed on a) PDS (0.3), b) PDVBF-0.05, c) PDSF-0.01, d) PDSF-0.05, e) PDSF-0.1, and f) PDSF-0.2.

lower the PA value, the stronger the acid strength. Clearly, the amount of grafted $-SO_2CF_3$ has a significant effect on the acid properties. If the $-SO_2CF_3$ group was grafted (PDVBF-0.05; Figure 3 b), only weak acid sites were found. The ³¹P chemical shift for the PDS (0.3) catalyst was 83.5 (60%) and 79 ppm (40%; Figure 3 a). PDSF-x catalysts functionalized with different amounts of CF₃SO₃H revealed strong acid sites with $\delta^{^{31}p} = 79$

(PDSF-0.01, 32%), 82 (PDSF-0.05, 83%), 83 (PDSF-0.1, 22%), and 81.5 ppm (PDSF-0.2, 12%), close to the threshold of superacidity (δ^{μ} = 85.3 ppm), which indicates that the interaction between F and S species has a crucial impact on the acidity.^[33] If we compare PDSF-0.05 and PDS (0.3), the ratio of strong acid sites increased significantly after modification with -SO2CF3 (from 60 to 83%). However, upon the introduction of excess -SO₂CF₃ (Figure 3 e and f), the spectra of the samples exhibited a broad overlapped ³¹P resonance peak that spanned from approximately 54 to 85 ppm, and the proportion of superacidity was reduced significantly because of the inhomogeneous distribution of the acid sites.^[34] Combined with the results obtained by using acid-base titration and N₂ adsorption-desorption (Table 1), we observe that the acidic ion-exchange capacity, specific surface area, and pore volume of PDSF-0.1 and PDSF-0.2 all decreased compared to those of PDS (0.3). This may be because excess -SO₂CF₃ results in pore blockage and the acid sites are not accessible to the probe molecules.

Thermogravimetric analysis results of various catalysts are shown in Figure 4. There are three weight-loss steps that can be attributed to the release of water (< 250 °C), the decomposition of functional groups (290–410 °C), and the decomposition of the polymer matrix (410–600 °C).^[26] Clearly, PDSF-0.05 has a better thermal stability than the commercial resins Amberlyst-15 and Nafion (one of the most stable commercial resins). Moreover, from the differential thermogravimetric analysis (DTG) results, the decomposition temperature of PDSF-0.05 (520 °C) was higher than that of PDVB (475 °C) and PDS (0.3) (500 °C). This may be because of the introduction of a strong electron-withdrawing group ($-SO_2CF_3$) that forms hydrogen bonds between H and F to stabilize the polymer texture.^[35] Liu et al.^[30] and Sun et al.^[33] drew similar conclusions.

Catalytic performance in the dehydration of sorbitol to isosorbide

The catalytic activity of the PDSF-*x* catalysts was evaluated in the conversion of sorbitol to isosorbide (Table 2). As water will have a negative effect on solid acid catalysts,^[36] vacuum conditions were used to remove the generated water quickly.



Figure 4. a) Thermogravimetric and b) DTG profiles of Nafion, Amberlyst-15, PDSF-0.05, PDS (0.3), and PDVB.



[b] Determined by using HPLC with an Aminex HPX-87H column at 60 $^\circ C$ (0.6 mLmin $^{-1}$, degassed $0.005\, M$ H_2SO_4 solution as eluent). [c] The TOF value is calculated from the results of acid-base titration. [d] Undetectable.

Optimization of the reaction conditions

The reaction conditions were optimized, and the results are listed in Figure 5. The yield of isosorbide increases gradually with an increase of the reaction time (Figure 5a). The best cat-

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alytic performance is achieved over PDSF-0.05 as a result of its large specific surface area, good hydrophobicity, and uniform acid distribution. Meanwhile, despite the higher amount of F species on PDSF-0.15 and PDSF-0.2, their catalytic performance is poor, which may result from their low specific surface area, small pore size, and low hydrophobicity. Our results show that an appropriate pore structure and surface properties are beneficial for the free access of the reactants to the active sites on the inner and outer surfaces. This conclusion is consistent with those reported previously.^[13a, 30]

Then, the reaction conditions for the PDSF-0.05 catalyst were optimized. A high amount of catalyst (3 wt%) leads to fast and complete sorbitol conversion (Figure 5 b). However, the subsequent increase in byproducts and humins leads to a low yield of isosorbitol. Finally, 2 wt% was selected as the optimum amount of catalyst.

Next, the influence of the temperature on the reaction of sorbitol was explored (Figure 5 c). The initial slope of the time-yield curve increases gradually as the reaction temperature increases, which indicates that temperature has an important influence on the reaction rate. A low temperature is not conducive to the rapid production of isosorbide, for example, if the temperature is between 110 and 130 °C, the yield of isosorbide increases very slowly. Additionally, a high reaction temperature favors the polymerization reaction.

temperature favors the polymerization reaction. Therefore, 140°C was chosen as the optimum evaluation temperature. The time-conversion/selectivity plot for sorbitol dehydration

to isosorbide over PDSF-0.05 is shown in Figure 5d. Basically, the reaction equilibrium of sorbitol dehydration is reached at a reaction time of 8 h. The conversion of sorbitol was 100%, and the selectivity of isosorbide was 80%.

Catalytic performance of PDSF-x

In the absence of the catalyst (Table 2, Entry 1), isosorbide was not detected after 8 h. With PDVBF-0.05 (Table 2, Entry 2), although the conversion was up to 95.3%, the yield of isosorbide was still as low as 23.9%, similar to that of PDS (0.3) (conversion 96.1%, yield 57.8%; Table 2, Entry 3). The two commercial resins, Amberlyst-15 and Nafion (Table 2, Entries 10 and 11), exhibited a very poor selectivity for the target product. In contrast, the PDSF-x catalysts show a good catalytic performance (Table 2, Entries 4-8), and with an increase of the amount of -SO₂CF₃ added, the isosorbide yield increased first and then decreased to reach a maximum at x = 0.05. The main products were isosorbide and 1,4-dehydrated sorbitol, trace 1,5-dehydrated sorbitol, and 2,5-mannitan. The undetermined products are defined as "Others". Among the catalysts, PDSF-0.05 has the highest turnover frequency (TOF) of 231.5 h^{-1} , higher than that of H_2SO_4 (219.4 h⁻¹), Amberlyst-15 (22.2 h⁻¹), and Nafion (39.2 h⁻¹). Additionally, compared with various reported catalysts, PDSF-0.05 gives a better catalytic activity and higher TOF value (detailed comparisons are listed in Table S1).



Figure 5. a) Time–yield plot for sorbitol dehydration to isosorbide over PSDF-x. Reaction conditions: sorbitol (25 g), catalyst (0.5 g, 2 wt%), 140 °C, 0.3 bar, 1200 rpm. b) Time–conversion/yield plot for sorbitol dehydration to isosorbide over different amounts of PSDF-0.05. Reaction conditions: sorbitol (25 g), catalyst (1, 2, and 3 wt%), 140 °C, 0.3 bar, 1200 rpm. c) Time–yield plot for sorbitol dehydration to isosorbide over 2 wt% PSDF-0.05 at different temperatures. Reaction conditions: sorbitol (25 g), catalyst (0.5 g, 2 wt%), 110–160 °C, 0.3 bar, 1200 rpm. d) Time–conversion/selectivity plot for sorbitol dehydration to isosorbide over 2 wt% PSDF-0.05. Reaction conditions: sorbitol (25 g), catalyst (0.5 g, 2 wt%), 110–160 °C, 0.3 bar, 1200 rpm. d) Time–conversion/selectivity plot for sorbitol dehydration to isosorbide over 2 wt% PSDF-0.05. Reaction conditions: sorbitol (25 g), catalyst (0.5 g, 2 wt%), 140 °C, 0.3 bar, 1200 rpm.

Compared to PDSF-0.05, less F species grafting (PDSF-0.01) led to weakened acidity, which may be the reason for poor catalytic activity. Notably, for PDSF-0.05, the amount of humins (9– 16%) was significantly lower than that over PDSF-0.1/0.15/0.2, which may be because of the hydrophobic microenvironment provided by the polymer substrate. Moreover, the large specific surface area, pore volume, and pore diameter facilitate the transport of reactants and products. Additionally, excessive grafting of strong electron-absorbing groups may lead to a large amount of byproducts, therefore, the acid strength should be in an appropriate range.

Catalyst reusability

The stability of PDSF-0.05 was investigated. The used PDSF-0.05 catalyst was activated as follows. Briefly, the solid catalyst was separated from the reaction mixture by filtration. Then, the recovered catalyst was washed thoroughly with a large amount of ethanol and deionized water to remove the adsorbed substances on the surface followed by drying under vacuum at 50 °C for 3 h. Thereafter, the catalyst was activated with 0.1 M H₂SO₄ for 4 h, washed with deionized water until neutral, and dried at 50 °C for 3 h before the next use.

No significant deactivation was found even after five cycles (from 80 to 75%) under the investigated conditions, which indicates that PDSF-0.05 is stable for the reaction (Figure 6).

Elemental analysis, N₂ adsorption–desorption, and FTIR spectroscopy were employed to study the properties of the spent catalyst. The values of the textural properties of PDSF-0.05 recycled five times decreased slightly (485 vs. 427 m^2g^{-1} , 0.63 vs. 0.49 cm³g⁻¹, 6.08 vs. 5.24 nm; Table 1, Entry 9 and Figure S7).



Figure 6. Reusability of PDSF-0.05 in sorbitol dehydration to isosorbide. Reaction conditions: sorbitol (25 g), catalyst (2 wt %), 140 °C, 0.3 bar, 8 h.

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The FTIR spectrum of the spent catalyst showed the same characteristic peaks as that of the fresh one, but the absorption peak of C–S was weakened slightly, which is consistent with the results of elemental analysis (Table 1, Entry 9). The slow decrease in activity may be caused by the gradual loss of the acid groups.

Possible reaction mechanism for the conversion of sorbitol over PDSF-x

To understand the reaction pathway of sorbitol dehydration over the PDSF-x catalysts, the selectivity to sorbitol was studied (Figure 7). For all catalysts, 1,4-sorbitan is formed as the main product, the selectivity of which reached 95% at low conversion (<20%; Figure 7 a). With the increase of conversion, the selectivity to 1,4-sorbitan decreases gradually, and the selectivity to isosorbide increases. At a high conversion (>90%; Figure 7b), isosorbide becomes the main product. These results indicate that isosorbide formation is divided mainly into two steps: the formation of 1,4-sorbitan (step I) followed by further dehydration to obtain isosorbide (step II). The selectivity to isosorbide over PDSF-0.05 was higher than that over the other catalysts at the same conversion (>90%; Figure 7b),



Figure 7. Selectivity to a) 1,4-sorbitan and b) isosorbide versus sorbitol conversion over various catalysts. Reaction conditions: sorbitol (25 g), catalyst (0.5 g, 2 wt %), 140 °C, 6 h, 0.3 bar, 1200 rpm.

which indicates that the PDSF-0.05 catalyst could promote the 1,4-sorbitan dehydration reaction more efficiently. The lower selectivity over PDSF-0.1/0.15/0.2 may result from the excessive amount of grafted F species that led to the low specific surface area and pore size of the catalysts, that is, reactant and product transport were inhibited to result in an increase of the formation of byproducts during the rapid conversion of sorbitol.^[13e] In addition, the poor catalytic activity of PDSF-0.01 may be caused by the lower grafting amount of F species and its low acid strength. Moreover, the hydrophobicity of the catalyst can influence the dehydration reaction of sorbitol (a polar substance) because of the weak affinity between the reactant and the catalyst surface, that is, the low selectivity of 1,4-sorbitan over PDSF-0.01 (Figure 7a) may also be affected by the hydrophobicity.

To compare the relative kinetics of the sorbitol dehydration reaction of three catalysts (PDSF-0.05, PDS(0.3), and H₂SO₄), the reaction was performed at different temperatures (130-150 °C) with the same amount of catalyst active sites. All the calculations and data (k_1 , k_2 , k_{all} , and E_a) are presented in the Supporting Information. The rate constant of PDSF-0.05 ($k_{all} = 0.78/$ 1.45/1.71 h⁻¹) is higher than that of PDS (0.3) ($k_{all} = 0.54/0.58/$ 0.80 h⁻¹) and H₂SO₄ ($k_{all} = 0.70/1.15/1.27$ h⁻¹; Table S2). In addition, the order of the activation energy for the three catalysts was all $E_{a2} > E_{a1}$, which indicates that the second step of the sorbitol dehydration reaction is more difficult. The activation energy of PDSF-0.05 ($E_{a1} = 72 \text{ kJ mol}^{-1}$, $E_{a2} = 87 \text{ kJ mol}^{-1}$) is higher than that of H_2SO_4 ($E_{a1} = 64 \text{ kJmol}^{-1}$, $E_{a2} = 66 \text{ kJmol}^{-1}$), which indicates the advantages of homogeneous over heterogeneous catalysts. The activation energy of PDSF-0.05 ($E_{a1} =$ 72 kJ mol⁻¹, E_{a2} = 87 kJ mol⁻¹) is lower than that of PDS (0.3) $(E_{a1} = 80 \text{ kJ mol}^{-1}, E_{a2} = 89 \text{ kJ mol}^{-1})$, which indicates that a high acid strength is beneficial for the sorbitol dehydration reaction.

Conclusion

A series of polydivinylbenzene solid acid catalysts modified by sulfonic acid and trifluoromethanesulfonic acid groups (PDSFx) catalysts with different acid strengths were synthesized and showed a good catalytic performance in sorbitol dehydration to isosorbide. A complete conversion of sorbitol, 80% isosorbide yield, and high turnover frequency (231.5 h⁻¹) were obtained under mild reaction conditions (140°C without solvent) over PDSF-0.05. Meanwhile, the recyclability of PDSF-0.05 is excellent (75% isosorbitol yield after five recycles). Moreover, an excessive grafting of F species would lead to the blockage of the catalyst channels and decrease the amount of exposed active sites. Moreover, the catalytic performance is related closely to the amount of acid sites accessible to the reactants. Therefore, an appropriate grafting amount of F species is necessary. In addition, the sorbitol dehydration reaction was confirmed to occur in two key steps (sorbitol \rightarrow 1,4-sorbitan \rightarrow isosorbide). Kinetic analysis showed that an increase in acid strength accelerated the rate of sorbitol dehydration. The asprepared PDSF-0.05 catalyst has the potential to substitute traditional mineral acids to catalyze the dehydration of sorbitol to isosorbide.



Experimental Section

Materials and methods

Materials

Unless otherwise noted, all commercial chemicals were used without further purification: tetrahydrofuran (THF, 99%, Aladdin), 2,2azobis(isobutyronitrile) (AIBN, 99%, Aladdin), trifluoromethanesulfonic acid (CF₃SO₃H, 98%, Aladdin), sodium *p*-styrenesulfonate hydrate (SPSS, C₈H₇NaO₃S·xH₂O, 90%, Aladdin), sodium chloride (Tianjin Tianli Chemical Reagent Co., Ltd.), sulfuric acid (98%, Tianjin Tianli Chemical Reagent Co., Ltd.), ethanol absolute (Sinopharm Chemical Reagent Co., Ltd.), divinylbenzene (DVB, 80%, Macklin Biochemical Co., Ltd.), sodium hydroxide (Tianjin Hengxing Chemical Reagent Co., Ltd.), Amberlyst-15 (Acros Organics). For the catalytic activity tests we used: D-sorbitol (98%, Aladdin), isosorbide (98%, Aladdin), 3,6-anhydro-D-galactose (295%, Aladdin), 1,5-anhydro-p-glucitol (Aladdin), 1,4-anhydro-sorbitol (TRC Canada), and 2,5-anhydro-D-glucitol (J&K Chemical Ltd.). The divinylbenzene (DVB) used in the catalyst synthesis was washed with sodium hydroxide solution (5%) to remove the polymerization inhibitor.

Catalyst Preparation

PDVB-SO₃H (PDS)

The functional mesoporous material PDVB–SO₃H was obtained by the hydrothermal synthesis of DVB and SPSS followed by ion exchange with dilute sulfuric acid. The molar ratio of DVB, SPSS, AlBN, THF, and H₂O was 1/0.96/0.02/16.1/7.23. Typically, DVB (2 g) and SPSS (0.96 g) were added to a solution that contained AlBN (0.05 g), THF (20 mL), and H₂O (2 mL). After it was stirred at RT for 3 h, the solution was transferred to an autoclave and treated hydrothermally at 100 °C for 24 h. Then, the white solid was evaporated at RT for 48 h to obtain PDSNa. Furthermore, PDSNa (1 g) was treated with 1 m sulfuric acid (100 mL) in ethanol for 24 h to obtain PDVB–SO₃H (PDS).^[13a, 26] The synthesis of the superhydrophobic mesoporous network PDVB was similar to that of PDS except that SPSS was not added.

PDVB-SO₃H-SO₂CF₃ (PDSF-x)

The polymer solid superacid PDSF-x was obtained by grafting different amounts of the strong electron-withdrawing group $-SO_2CF_3$ on the PDS precursor. Typically for PDSF-0.05, PDS (3 g) was added to a flask that contained toluene (100 mL), and the temperature was increased rapidly to 100 °C. Then, CF₃SO₃H (5 mL) was dropped slowly into the above solution. After it was stirred for 24 h, the PDSF-0.05 catalyst was washed with a large amount of CH₂Cl₂ followed by Soxhlet extraction for 48 h. The sample was dried under vacuum at 80 °C. The synthesis of the other PDSF-x (x = 0.01, 0.1, 0.15, 0.2) catalysts was the same except for the amount of CF₃SO₃H (1, 10, 15, 20 mL).^[30]

For comparison, a PDVBF-0.05 catalyst that contained only one acid group $(-SO_2CF_3)$ was synthesized in which PDVB was used as the precursor, and then the grafting method of the $-SO_2CF_3$ group was the same as that used for PDSF-0.05.

Characterization

 $N_{\rm 2}$ isotherms were measured at $-196\,^\circ C$ by using a Micromeritics Tristar II (3020) instrument system. The surface area and pore sizes

distribution were calculated by using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Before adsorption, all samples were outgassed for 10 h at 150 $^{\circ}$ C under vacuum.

The amount of grafted acid groups on the polymer network was assessed by calculation of the S content by using a Vario EL CUBE elemental analyzer (CHNS). For all catalysts, S only exists in the - SO₃H and -SO₂CF₃ groups, so the S content represents the content of acid groups.

The acid exchange capacity of the solid acid catalysts was determined by using acid-base titration. Typically, catalyst (0.05 g) was dried at 100 °C for 10 h and then stirred in NaCl (2 m, 50 mL) solution for 12 h until equilibrium was reached. The solution was then sonicated for 30 min. The sample was collected by filtration and washed, and the free H⁺ in the filtrate was titrated by standard sodium hydroxide solution (0.01 m) with phenolphthalein as an indicator.

XRD patterns were measured by using a DX-2700 with a monochromator and CuK_{α} radiation ($\lambda = 1.54184$ Å) at 40 kV and 30 mA. The scanning rate was 4° min⁻¹ in the range $2\theta = 5-85^{\circ}$.

The morphology of the catalyst samples was investigated by using SEM at 5 kV by using an Extreme-resolution Analytical Field Emission SEM (Tescan Mira 3).

TEM images were recorded by using a JEM-2100F high-resolution transmission electron microscope operated at an acceleration voltage of 200 kV.

Contact angles (CA) were tested by using a SL200B, Kino, USA.

Adsorption isotherms of water were performed by using a BEL-SORP-max instrument at 25 °C. The samples (\approx 25 mg) were outgassed for 10 h at 150 °C before the measurements.

FTIR spectra were recorded by using a Nicolet Nexus 470 FTIR Spectrometer. The range and resolution of acquisition were 4000– 400 cm^{-1} with 64 scans and 2 cm⁻¹, respectively. A self-supporting wafer of each sample was diluted with KBr.

To analyze the chemical composition in all samples, XPS was performed by using a Thermo Fisher ESCALAB 250 xi instrument with AIK, radiation (1486.6 eV).

Thermogravimetric analysis was performed by using a Rigaku Thermo plus Evo TG 8120 in a flow of dry air (30 mLmin^{-1}). The heating rate was $10^{\circ}\text{Cmin}^{-1}$ (RT to 800°C).

Solid-state ³¹P NMR spectra were recorded by using a Bruker Avance 600 MHz wide-bore spectrometer equipped with a 4 mm double-resonance probe. Details of the TMPO adsorption process have been reported previously.^[32] Before the tests, the samples were pretreated as follows. To remove the water adsorbed on the surface of the sample completely, the test temperature was increased gradually to 130°C for 12 h under vacuum (10⁻³ Pa) followed by cooling. Subsequently, a completely dry sample was dispersed in a mixture of TMPO (known in content) and CH₂Cl₂ in a N₂-filled glovebox, followed by the removal of CH₂Cl₂ at RT. The sample was then heated at 170°C for 8 h to ensure the uniform adsorption of probe molecules in the sample channels. Before testing, the sealed sample tube was opened and transferred to the NMR rotor sealed by a gas-tight Kel-F cap in a N₂-filled glovebox. A Larmor frequency of 600 MHz and a typical $\pi/2$ pulse length of 4.6 µs were adopted. For the ³¹P MAS NMR spectroscopy experiment, the single pulse sequence was equivalent to ca. $\pi/4$ (for

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15 s). The chemical shifts were referenced to $(NH_4)_2HPO_4$ ($\delta = 1.0$ ppm), and the MAS frequency was 10 kHz.

EPR spectra were obtained by using an EMXPLUS10/12 working in the X-band (9.84 GHz) at 25 $^\circ\text{C}.$

Catalyst tests

Sorbitol dehydration reaction

The sorbitol dehydration reaction was conducted in a 250 mL three-necked flask. Typically, sorbitol (25 g) was added to the three-necked flask and heated to the desired temperature to obtain a clear liquid (melted sorbitol without solvent), after which a certain amount of the catalyst was added to the reaction system (the reaction time was recorded as t=0). The reaction was performed under vacuum (0.3 bar), and the stirring speed was 1200 rpm. Each reaction was repeated at least twice.

Product analysis

The reaction products were removed from the reactor at intervals, cooled rapidly to RT, and diluted with deionized water. The solution was filtered through an organic filter (0.22 μ m) before it was analyzed by using HPLC (LC-10Avp) equipped with an Aminex HPX-87H column (diameter 7.8 mm, 300 mm, 9.0 μ m) and a differential refraction detector (RID-10A). The eluent was a 0.005 μ solution of H₂SO₄ (0.6 mL min⁻¹), and the column temperature was 60 °C. The mass balance for all the reactions was higher than 96%. The specific product analysis method is consistent with our previous work.^[13a] Equations (1) and (2) were used to calculate the sorbitol conversion (C_{sorbitol}) and product selectivity (S_x):

$$C_{\text{Sorbitol}}(\%) = \frac{\text{moles of reacted sorbitol}}{\text{moles of initial sorbitol}} \times 100 \tag{1}$$

$$S_{x}(\%) = \frac{\text{moles of product } x}{\text{moles of all products}} \times 100$$
(2)

In which S_x stands for the selectivity of sorbitans or isosorbide. In the product analysis, we used the respective response factors for sorbitol and isosorbide. A trace amount of 3,6-sorbitan may be included in the detected 1,4-sorbitan as they were epimers that cannot be separated completely by using HPLC.^[10a,13h,17a,b,19] In addition, the selectivity of undetected products and humins was considered as $S_{Othersr}$ and $S_{Othersr} = 100\% - S_{Sorbitan} - S_{Isosorbide}$.

TOF values $[h^{-1}]$ were calculated by Equation (3):

$$TOF = \frac{n_{sorbitol} * C_{sorbitol}}{m_{catalyst} * N_{acid site} * t}$$
(3)

in which n_{sorbitol} stands for the amount of the reactant sorbitol [mol], C_{sorbitol} stands for the conversion of sorbitol (10–20%), m_{catalyst} stands for the mass of the catalyst [g], $N_{\text{acid site}}$ stands for the number of the acid sites obtained by acid–base titration [mmolg⁻¹], and the reaction time is represented by t [h].

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Conflict of interest

The authors declare no conflict of interest.

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FULL PAPERS

Hard graft: A series of polymeric solid acid catalysts (PDSF-x) is prepared by grafting strong electron-withdrawing groups (-SO₂CF₃) on a sulfonic acidmodified polydivinylbenzene (PDS) precursor. The effect of acid strength on sorbitol dehydration is investigated.



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Solvent-Free Production of Isosorbide from Sorbitol Catalyzed by a **Polymeric Solid Acid**