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1. Introduction

Although today coal, natural gas, petroleum, and other nonrenewable fossil resources supply most energy and chemicals,1 in the future decades these fossil resources are unlikely to meet the growing needs of humanity. Moreover, consumers and governments pay more and more attention to environmental issues and environment protection and are demanding renewable energy and products. With the development of conversion technology, abundant biomass resources have the potential to occupy the main position as feedstocks, particularly as renewable carbon sources for the production of fuels and chemicals.² One of those, the platform chemical 5-hydroxymethylfurfural (HMF) plays an important role in biobased energy, because HMF can be converted by effective methods into several useful acids, such as levulinic acid, 2,5-furandicarboxylic acid (FDA), and 5-hydroxy-4-keto-2-pentenoic acid,3 as well as the promising fuel 2,5-dimethylfuran (DMF).4 Several efforts toward HMF production have used edible carbohydrate-based biomass such as fructose and glucose, which are easy to convert into valuable products. However, their consumption for the manufacture of biofuels would cause a food deficiency, contrary to the case of

Porous solid acid with high Surface area derived from emulsion templating and hypercrosslinking for efficient one-pot conversion of cellulose to 5hydroxymethylfurfural

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This work addressed efficient one-pot conversion of cellulose to 5-hydroxymethylfurfural by porous solid acid in the presence of 1-ethyl-3-methyl-imidazolium chloride ([Emim]Cl). On the basis of stable water-inoil pickering high internal phase emulsions (HIPEs), porous solid acid (HC-PDVB-SS-SO₃H) was prepared by polymerizing divinylbenzene (DVB) and sodium *p*-styrenesulfonate (SS), succedent sulfonation in H₂SO₄ and hypercrosslinking process. HC-PDVB-SS-SO₃H with a stable network exhibited mesopores within a macropore structure, high BET specific surface area and more super-strong acid sites. To test catalytic activity, the reaction conditions were optimized *via* response surface methodology, and the sequence of the three variables affecting HMF yield followed the order, temperature > reaction time > amount of catalyst. By comparing with the other as-prepared porous solid acid, it can also be concluded that BET specific surface area and super-strong acid site both played key roles in cellulose conversion. Moreover, HC-PDVB-SS-SO₃H was very easily reused at least four times without significant loss of activity.

wood-based biomass (*e.g.*, cellulose).^{5,6} Unfortunately, improving the efficiency in cellulose convert into HMF is a challenge owing to the complex structure and difficulty of dissolving in general solvents.

In recent years, several studies have adopted various types of solid acid catalysts for the conversion of cellulose to HMF in ionic liquid because solid acid and ionic liquid possesses ultra strong acid strength and unique solubility for cellulose. For example, we fabricated two acid-chromic chloride bifunctionalized solid acid catalysts by grafting the -SO3H and Cr(m) onto the surface of treated attapulgite (ATP) and halloysite nanotubes (HNTs), and their catalytic activities were evaluated for the one-pot conversion of cellulose to 5-hydroxymethylfurfural (HMF) in an ionic liquid 1-ethyl-3-methylimidazolium chloride ([EMIM]-Cl).7 Very recently, we applied precipitation polymerization and Pickering emulsion polymerization combined with a sulfonation process for synthesizing two types of polymeric solid acid for cellulose conversion in [EMIM]-Cl, which showed a satisfying yield of HMF.8 Nevertheless, solid acids, which have a high yield of HMF, as well as a simple synthesis process in combination with easy recovery are also practically unavailable.

Recently, mesoporous solid acids⁹⁻¹³ have been widely used in HMF production, because of their high specific surface area and large pore volume. For example, Clayton *et al.*¹⁴ successfully obtained 29% HMF yields using a fixed bed porous metal oxide-based catalytic process in two liquid phases. Peng *et al.*¹⁵

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have prepared acidic large-pored mesoporous silica nanoparticles for a one-pot catalysis of cellulose to HMF with a low yield of 18%. Xiao's group successfully designed and synthesized a stable mesoporous polymeric solid acid for cellulose conversion.16 The excellent catalytic activity was determined for these mesoporous materials, but extra isolation steps for catalyst recycling mass and slow mass transfer to the active sites on the internal surface limited their further application.¹⁷ The mass transport limitations of a mesoporous solid acid can be overcome using macroporous polymers based on high internal phase emulsions (HIPEs), which possess very large pores (1-100 µm).18 HIPEs, as emulsions with a volume fraction of the droplet phase higher than 74%, provide a very convenient route to synthesize macroporous polymer supports (polyHIPEs) by polymerizing the monomers in the continuous phase.19 However, conventional polyHIPEs synthesized from surfactant stabilized HIPEs have poor mechanical properties and low surface area.²⁰ In the literature, it has been shown that the poor mechanical properties usually observed for poly-HIPEs can be improved by particle reinforcements, and one of the typical method was utilizing particle-stabilized HIPEs templates (Pickering HIPEs) to produce macroporous polymers. Bismarck's group²¹ made use of pickering HIPEs incorporated with small amounts of non-ionic polymeric surfactant to form a macroporous polyHIPEs with an open porous structure. To address the bottleneck of low surface area, an alternative technology is the development of extensive post polymerisation crosslinking of swollen or dissolved polymers, namely hypercrosslinking (HC).22 Krajnc and co-workers23 had successfully created micropores within macroporous monoliths by post polymerisation hypercrosslinking of styrene/ divinylbenzene polyHIPEs. Their work demonstrated that the hypercrosslinking process could significantly increase BET surface area, while retained the macroporous morphology, which is a typical of polyHIPEs materials.

Herein, a series of porous polymerized solid acids were successfully designed and produced by W/O Pickering HIPEs template method and a succedent hypercrosslinking process. First, the as-prepared hydrophobic silica particles and span 80 were both used to stabilize W/O Pickering HIPEs with an internal phase volume ratio of 84.8%. Then, Pickering HIPEs had an external phase containing divinylbenzene (DVB) monomer, and an internal phase containing DVB when the external phase containing sodium p-styrene sulfonate (SS) monomer were applied to fabricated porous materials PDVB and PDVB-SS, respectively. After sulfonation in 98% H₂SO₄, two porous polymerized solid acids PDVB-SO₃H and PDVB-SS-SO₃H were obtained. Moreover, the third solid acid HC-PDVB-SS-SO₃H was prepared by further hypercrosslinking reaction and sulfonation of PDVB-SS. Then, three polymerized solid acids were all characterized, and the catalytic activities were discussed in detail by optimizing the reaction time, temperature and catalyst loading amounts in catalyzing cellulose to HMF. HC-PDVB-SS-SO₃H with a large surface area, ultra strong acid strength and stable network possessed good recyclability and catalytic activity compared with PDVB-SO₃H and PDVB-SS-SO₃H.

2. Material and methods

2.1 Materials

1-Ethyl-3-methyl-imidazolium chloride ([EMIM]-Cl), cellulose (powder, ca. 50 micron), 5-hydroxymethylfurfural (HMF) (>99%), tetraethoxysilane (TEOS), divinylbenzene (DVB), 3methacryloxypropyltrimethoxysilane (KH-570) were supplied by Aladdin reagent Co., Ltd (Shanghai, China). 2,2'-Azo-bis-(2methyl-propionitrile) (AIBN, 99%), toluene, ethanol, methanol, n-hexane, Span 80, K₂SO₄, FeCl₃ (anhydrous), potassium persulfate (KPS), NH3·H2O (25 wt%), sodium p-styrene sulfonate (SS), 1,2-dichloroethane and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the other chemicals were supplied by local suppliers and used without further purification.

2.2 Instruments and characterization

FTIR spectra were measured with a Nicolet NEXUS-470 FTIR apparatus (U.S.A.). The morphology of the silica particles and the as-prepared solid acid catalysts were characterized by field emission scanning electron microscopy (SEM, JSM-7100F). Energy Dispersive Spectra (EDS) were obtained on a SEM instrument. XPS spectra were performed on a Thermo ESCALAB 250 with Al Ka radition at y = 901 for the X-ray source, the binding energies were calibrated using the C1s peak at 284.9 eV. Elemental composition was recorded by the vario EL III elemental analyzer (Elementar, Hanau, Germany). The acidic features of the samples were all measured according to NH₃ temperature-programmed desorption (NH₃-TPD) curves, which were recorded with a thermal conductivity detector (TCD, DAS-7000, Beijing, China). TGA of the samples were performed for powder (near 10 mg) using a Diamond TG/DTA instrument (Perkin-Elmer, U.S.A.) under a nitrogen atmosphere up to 800 °C at a heating rate of 5.0 °C min⁻¹. The water contact angle of silica particles were measured with the Optical Contact Angle Measuring Device (KSV CM200). A detailed test procedure is described as follows: 2.0 µL of deionized water was injected on the sample surface by a syringe pump, and then the images of the water droplet were obtained using the camera of the measuring device 30 s after the water droplet was formed on the sample surface. Finally, the these images were analyzed using the supplied software to determine the contact angle of the sample.

2.3 Synthesis of hydrophobic silica particles as stabilizers

Hydrophobic silica particles, which were used to stabilize W/O Pickering HIPEs, were synthesized *via* two steps: First, hydrophilic silica particles were prepared using the well-known hydrolysis and condensation reaction according to a modified Stöber's method.²⁴ 6.0 mL of TEOS was slowly injected into a uniform solution containing 90 mL ethanol, 10 mL H₂O and 3.14 mL 25 wt% NH₃·H₂O. Then, the mixtures were reacted for 1.0 h at 30 °C with mechanical stirring, and subsequently the reaction products were separated and washed several times with ethanol by centrifugation. Finally, the uniform sizes of hydrophilic silica particles were obtained by drying for 8.0 h at 40 $^\circ\mathrm{C}$ in a vacuum oven.

Second, the as-prepared hydrophilic silica particles were further modified with KH-570. In a typical run, hydrophilic silica particles (1.0 g), toluene (150 mL), H_2O (15 mL) and KH-570 (3.5 mL) were mixed and stirred for 24 h at 40 °C in a 250 mL three-neck flask. Subsequently, the reaction products were separated and washed with ethanol. Finally, hydrophobic silica particles were obtained by drying for 12 h at 40 °C in a vacuum drying oven.

2.4 Preparation of PDVB-SO₃H and PDVB-SS-SO₃H

PDVB-SO₃H was prepared by emulsion polymerization and a subsequent sulfonation process. The first step was the synthesis of porous PDVB polymers via a Pickering HIPEs template method, and the HIPEs recipes are listed in Table 1. A continuous phase was formed by stirring the hydrophobic silica particles (0.3 g), AIBN (0.04 g), DVB (3.0 mL) and span 80 (0.4 mL) in a 100 mL three-neck flask. Next, 16.8 mL of the internal aqueous phase comprised of K2SO4 (0.08 g) was gradually added with continuous stirring, and the stable W/O Pickering HIPEs were obtained. Then, the obtained Pickering HIPEs were transferred into a plastic centrifuge tube and polymerized in a circulating air oven at 60 °C. After 12 h, the as-prepared PDVB was washed with deionized water and acetone in turn, and then macroporous PDVB monoliths were dried at 80 °C for 12 h. The second step was grafting the above PDVB with -SO₃H by a sulfonation process. In brief, PDVB monoliths (1.0 g) and 98% H₂SO₄ (30 mL) were mixed and stirred at 70 °C for 12 h. Then, the reaction products were filtered and washed to remove the excess of H₂SO₄ using volumes of deionized water. Finally, PDVB-SO₃H was obtained after drying in vacuum at 80 °C for 3.0 h.

The preparation of PDVB-SS-SO₃H also had two steps, such as the fabrication of macroporous PDVB-SS monoliths and a subsequent sulfonation process. For the preparation of PDVB-SS, the SS (0.2 g) and KPS (0.04 g) were added into the internal aqueous phase (Table 1), and the other processes were the same as the formation of macroporous PDVB monoliths. Moreover, the sulfonation process was followed by the step described above. Finally, the obtained products were identified as PDVB-SS-SO₃H.

2.5 Preparation of HC-PDVB-SS-SO₃H

The preparation of HC-PDVB-SS-SO₃H included the post polymerisation hypercrosslinking of PDVB-SS and a subsequent sulfonation process. In a typical run, the as-prepared PDVB-SS (1.0 g) was swollen in 1,2-dichloroethane (40 mL) under N₂ for 3.0 h. Then, FeCl₃ (1.6 g) in 20 mL of 1,2dichloroethane was added into the mixture of PDVB-SS and 1,2-dichloroethane, and the reaction mixture was stirred for another 18 h at 80 °C. The resulting hypercrosslinked products were filtered and washed three times with water and methanol, and then washed with methanol in a Soxhlet extraction for 24 h. Subsequently, the products (HC-PDVB-SS) were dried under vacuum at 40 °C for 24 h. Next, the sulfonation process of HC-PDVB-SS was followed by the step described above. Consequently, the obtained products were identified as HC-PDVB-SS-SO₃H.

2.6 The conversion of cellulose to HMF and analysis of HMF

A typical procedure for the conversion of cellulose to HMF according to modified Wei's method²⁵ is detailed as follows. First, cellulose (0.1 g) and [EMIM]Cl (2.0 g) were heated with stirring at 125 °C for 30 min until a clear solution was formed, in order to destroy the degree of crystallization and regularity of the cellulose. Then, the as-prepared HC-PDVB-SS-SO₃H (45 mg) was added into the mixed solution, and was allowed to continue reacting for 2.0 h at 125 °C under continuous stirring. Next, the reaction was immediately quenched with cold water, and diluted 5000 times with deionized water. Finally, liquid samples were analyzed by a high performance liquid chromatography (HPLC) with an Agilent 1200 instrument. HMF was detected with a UV-vis detector at a wavelength of 283 nm. The column used was an Agilent TC-C18 Column (4.6 \times 250 mm, 5.0 mm). The mobile phase was mixed water and methanol with the volume ratio of 30:70, and the flow rate and column oven were set to 0.7 mL min⁻¹ and 25 °C, respectively. Moreover, the HMF content was obtained according to the standard curve method. In this work, the HMF yield was defined as the ratio of total mole number of carbon atoms of HMF (n_1) and total moles number of carbon atoms in initial cellulose loaded in the reactor (n_0) , which was expressed in eqn (1).

$$Y_{\rm HMF} \,(\%) = 100 \times (n_1/n_0) \tag{1}$$

3. Results and discussion

3.1 Fabrication of hydrophobic silica particles

The water contact angle images of hydrophilic and hydrophobic silica particles were shown in Fig. 1a and b, and it could be clearly observed that the water contact angles were

Table 1 Recipes of W/O Pickering HIPEs												
Samples	External orga	nic phase		Internal aqueous phase								
	DVB (mL)	AIBN (g)	Silica (g)	Span80 (mL)	Water (g)	K_2SO_4 (g)	KPS (g)	SS (g)				
PDVB-SO ₃ H PDVB-SS-SO ₃ H	3.0 3.0	0.04 0.04	0.3 0.3	0.4 0.4	16.8 16.8	0.08 0.08	0 0.04	0 0.2				



Fig. 1 Water contact angle images of hydrophilic (a) and hydrophobic (b) silica particles.

about 34.5° and 125.7°, respectively, suggesting that hydrophobic silica particles were successfully prepared by grafting vinyl groups on the surface of hydrophilic silica particles. Moreover, the proper water contact angle meets the requirement for stabilizing W/O Pickering HIPEs, which was proved by Binks's groups using the particles with the water contact angle of 123° to stabilize W/O pickering HIPEs.²⁶ Furthermore, the morphology of hydrophilic and hydrophobic silica particles was both observed by SEM, which is shown in Fig. 2a and b, respectively. Hydrophilic and hydrophobic silica particles were both regular sphere-shaped, and their sizes were 200 \pm 20 nm and 250 \pm 20 nm, respectively. This phenomenon of increased sizes further confirmed that the vinyl groups were grafted onto the surface of hydrophilic silica particles.



Fig. 2 SEM images of hydrophilic silica particles (a), hydrophobic silica particles (b), PDVB-SO₃H (c), PDVB-SS-SO₃H (d) and HC-PDVB-SS-SO₃H (e).

3.2 Characterizations of porous polymerized solid acid

3.2.1 Morphological features and porous structure of catalysts. Fig. 2 also shows the SEM images of PDVB-SO₃H (c), PDVB-SS-SO₃H (d) and HC-PDVB-SS-SO₃H (e). Clearly, PDVB-SO₃H (Fig. 2c) displayed a well-defined open-cell structure (void size of 12 \pm 2 μ m) and interconnecting pore throat sizes in the range 0.5-3.0 µm. However, PDVB-SS-SO₃H (Fig. 2d) had a close-cell structure with few interconnecting pore throats, and a polymer film covered region between two voids. The mechanism for the formation of pore throat in polyHIPEs indicates that the films for the separation of the droplets in HIPEs must be sufficiently thin to break and form pore throats.²⁷ Moreover, the polymerized SS monomer layer in the internal phase of PDVB-SS-SO₃H increased the thickness of the contact domains between the neighboring droplets during polymerization, and the function against coalescence resulted in the close-cell structure. It was also determined that the void size of PDVB-SS-SO₃H (30 to 50 µm) was larger than that of PDVB-SO₃H. It was possibly because dissolved SS monomers in the internal phase of PDVB-SS-SO₃H brought about high interfacial energy and low electric potential in the oil-water interface, which was of beneficial for increasing the sizes of HIPEs droplets. Compared with PDVB-SS-SO₃H, no significant change in the morphological features was observed for HC-PDVB-SS-SO₃H (Fig. 2e). This result was also investigated and proved by Krajnc's group. They suggested that post polymerisation crosslinking involved reactions between pre-formed polymer chains, and the morphological feature of the material was slightly affected.17

Porous structure has a remarkable effect on the catalytic effect, and the nitrogen adsorption–desorption isotherms of HC-PDVB-SS-SO₃H (a), PDVB-SS-SO₃H (b) and PDVB-SO₃H (c) are listed in Fig. 3. As shown in Fig. 3, they all displayed a typical type-IV isotherm with a step capillary condensation in the relative pressure range of 0.1–0.9, and this type of isotherm was in agreement with the presence of obvious mesoporosity. Moreover, the porosity property of HC-PDVB-SS-SO₃H, PDVB-SS-



Fig. 3 Nitrogen adsorption–desorption isotherms of HC-PDVB-SS-SO $_3$ H (a), PDVB-SS-SO $_3$ H (b), and PDVB-SO $_3$ H (c).

Samples	$V_{\rm t}^{a} \left(\rm cm^{3} g^{-1} \right)$	$D_{\rm BJH}^{b}({\rm nm})$	$S_{\rm BET}^{\ \ c} \left({ m m}^2 \ { m g}^{-1} ight)$	Acid strength (°C)	Acid amounts $(\mu mol g^{-1})$	Total acidity $(\mu mol \ g^{-1})$	HMF (%)
PDVB-SO₃H	0.05	14.19	30.24	250	50	235	22.3^{d}
5				378	116		
				557	69		
PDVB-SS-SO ₃ H	0.13	10.67	80.06	285	49	313	25.2^{d}
				369	95		
				518	169		
HC-PDVB-SS-SO ₃ H	0.20	5.94	323.95	604	104	237	28.9^{e}
				706	133		

 Table 2
 The porosity properties, acidic properties and catalytic efficiency of the catalysts

 a V_t is the total pore volume determined at the relative pressure of 0.99. b D_{BJH} is BJH pore diameter calculated by the desorption branches of the nitrogen sorption isotherms. c S_{BET} is the BET specific surface area. d The reaction condition are 2.0 h, 130 °C and 50 mg of catalyst. e The reaction condition are 1.75 h, 125 °C and 45 mg of catalyst.

SO₃H, and PDVB-SO₃H are listed in Table 2. Clearly, the BET surface area (323.95 $\text{m}^2 \text{g}^{-1}$) and pore volume (0.20 $\text{cm}^3 \text{g}^{-1}$) of HC-PDVB-SS-SO₃H were obviously higher compared to those of PDVB-SS-SO₃H (80.06 m² g⁻¹, 0.13 cm³ g⁻¹), and PDVB-SO₃H $(30.24 \text{ m}^2 \text{ g}^{-1}, 0.05 \text{ cm}^3 \text{ g}^{-1})$. The low surface area was found for highly permeable macroporous PDVB-SO₃H polymers, and this result demonstrated that PDVB-SO₃H possessed a very less amount of mesopores. Although a close-cell structure was obtained for HC-PDVB-SS-SO₃H, a significant enlargement of the amount of mesopores in the material was determined resulting from post polymerisation hypercrosslinking. Nevertheless, the BJH pore diameter (5.94 nm) of HC-PDVB-SS-SO₃H was lower compared to PDVB-SS-SO₃H (10.67 nm), and PDVB-SO₃H (14.19 nm), which could be attributed to the presence of SS monomers, which might block the mesopores and increase the density of the network in the hypercrosslinking process.

3.2.2 Chemical composition of catalysts. Fig. 4 shows the FTIR spectra of PDVB-SO₃H (a), PDVB (b), regenerated HC-PDVB-SS-SO₃H (c), HC-PDVB-SS-SO₃H (d) and PDVB-SS-SO₃H (e). The peaks at 1456 cm⁻¹ associated with benzene ring, and 1107 cm⁻¹ assigned to Si–O–Si antisymmetric stretching vibration could both be clearly observed in all the samples,²⁸



Fig. 4 FTIR spectra of PDVB-SO₃H (a), PDVB (b), regenerated HC-PDVB-SS-SO₃H (c), HC-PDVB-SS-SO₃H (d) and PDVB-SS-SO₃H (e).

suggesting the presence of silica particles and monomers such as DVB or SS. In addition, the peak at 1039 cm⁻¹ attributed to C–S bond, and 1170 cm⁻¹ belonging to $-SO_3H$ groups were also clearly observed in the samples of PDVB-SO₃H, regenerated HC-PDVB-SS-SO₃H, HC-PDVB-SS-SO₃H and PDVB-SS-SO₃H, confirmed that the sulfonic groups were successfully grafted onto the benzene rings of the monomers.

Energy dispersive spectrometry (EDS) analysis of PDVB, PDVB-SO₃H, and PDVB-SS-SO₃H are listed in Fig. 5a-c, respectively. When comparing Fig. 5a with b, the peak of the element S appeared in the sample of PDVB-SO₃H, and the same phenomenon was also determined in the sample of PDVB-SS-SO₃H when comparing Fig. 5a with c, which suggested that -SO₃H groups were successfully grafted onto the surface of PDVB via the sulfonation process. Furthermore, it could be determined that the peak of the element S in the sample of PDVB-SS-SO₃H was stronger compared to PDVB-SO₃H, and the amount of S was also more than that of PDVB-SO₃H. Thus, it could be emphasized that PDVB-SS-SO3H had a PSS layer, which resulted in more -SO₃H groups in the sample of PDVB-SS-SO₃H. Furthermore, the results of the elemental analysis of PDVB, PDVB-SO₃H and PDVB-SS-SO₃H are all shown in the corresponding figures. Moreover, the amount of S in the sample of PDVB-SO₃H (0.65%) was increased to 2.28% in the sample of PDVB-SS-SO₃H, and S was not observed in PDVB. These results agree with the results of EDS analysis.

Fig. 6 shows the X-ray photoelectron spectroscopy (XPS) measurements of PDVB-SO₃H and HC-PDVB-SS-SO₃H. Clearly, PDVB-SO₃H and HC-PDVB-SS-SO₃H both showed the signals of S, C, Si and O, possibly indicating the presence of $-SO_3H$ groups and hydrophobic silica particles in these samples. Correspondingly, the highly resolved XPS spectrum of C1s showed signals at around 284.7 eV, which were associated with C–S bond in these samples. This result further proved the successful introduction of $-SO_3H$ into the network of these samples, and $-SO_3H$ groups would contribute to increase the acid strength of these solid acids.²⁹ Moreover, the signal of S2p of PDVB-SO₃H and HC-PDVB-SS-SO₃H were found at the same position with a binding energy of 169 eV, suggesting that the hypercrosslinking process of HC-PDVB-SS-SO₃H had no obvious effect on the



Fig. 5 Energy dispersive spectra (EDS) and elemental analysis of PDVB (a), PDVB-SO₃H (b) and PDVB-SS-SO₃H (c).



Fig. 6 X-ray photoelectron spectroscopy measurements of survey (a) C1s, (b) S2p, (c) Si2p, (d) of PDVB-SO₃H and HC-PDVB-SS-SO₃H.

introduction of $-SO_3H$ groups, and the results also supported the fact that the HC-PDVB-SS-SO₃H catalyst possessed a rigid network structure and good chemical stability. Furthermore, the peak position of Si2p of PDVB-SO₃H and HC-PDVB-SS-SO₃H were both at 102.2 eV, and the phenomenon showed that hydrophobic silica particles might not be involved in other reactions except in the emulsifying process.

Fig. 7 showed the TGA curves of PDVB-SO₃H (a), HC-PDVB-SS-SO₃H (b), and PDVB-SS-SO₃H (c). Slight weight loss of PDVB-SO₃H (6.78%), HC-PDVB-SS-SO₃H (9.09%) and PDVB-SS-SO₃H (11.29%) within the initial temperature range (<150 °C) could be observed, which could be attributed to the loss of H₂O in these samples.³⁰ With the temperature increased to 450 °C, the obvious weight losses of PDVB-SO₃H (11.37%),



Fig. 7 TGA curves of PDVB-SO_3H (a), HC-PDVB-SS-SO_3H (b) and PDVB-SS-SO_3H (c).

HC-PDVB-SS-SO₃H (16.57%), and PDVB-SS-SO₃H (17.64%) resulting from decomposition of $-SO_3H$ groups could also be seen.³¹ Interestingly, it could be found that the more $-SO_3H$ groups the catalyst had, the higher adsorption content of water, which suggested that $-SO_3H$ groups provided more hydrophilic surface. When the temperature further increased to 800 °C, PDVB-SO₃H, HC-PDVB-SS-SO₃H and PDVB-SS-SO₃H had a significant weight loss with 46.75%, 36.76%, and 30.76%, respectively, due to the destruction and decomposition of spatial structure of catalysts. At 800 °C, the remaining mass for catalysts may be put down to rigid silica particles and residual carbon by calcining polymers.³²

3.2.3 The acidic properties of catalysts. The acidic features of PDVB-SO₃H, PDVB-SS-SO₃H and HC-PDVB-SS-SO₃H catalysts were determined by use of NH₃-TPD. Additionally, the type of distinguishing acid sites was based on desorption temperatures of NH₃, and 150–250 °C, 250–350 °C, 350–500 °C and >500 °C were measured as weak, medium, strong and super-strong acid sites, respectively.³³ As shown in Fig. 8, it can be clearly seen that

medium, strong and very strong acid sites existed in PDVB-SO₃H and PDVB-SS-SO₃H, but HC-PDVB-SS-SO₃H possessed only super-strong acid sites that can also be readily observed. Moreover, the areas of the peak represented the amount of acidic sites were further calculated and summarized in Table 2. The total acidic amount of 235 μ mol g⁻¹ for PDVB-SO₃H (*i.e.* respective acidic amounts of 50 μ mol g⁻¹, 116 μ mol g⁻¹ and 69 μ mol g⁻¹ for the acidic strengths of 250 °C, 378 °C and 557 °C) was less than that of 313 μ mol g⁻¹ for PDVB-SS-SO₃H (*i.e.* respective acidic amounts of 49 μ mol g⁻¹, 95 μ mol g⁻¹ and 169 μ mol g⁻¹ for the acidic strengths of 285 °C, 369 °C and 518 °C), and 237 μ mol g⁻¹ for HC-PDVB-SS-SO₃H (*i.e.* respective acidic amounts of 104 μ mol g⁻¹ and 133 μ mol g⁻¹ for the acidic strengths of 604 °C and 706 °C). Moreover, it could also be simply proved that the results of total acidic amount were identical with the amounts of -SO₃H groups resulting from TGA analysis. Furthermore, the acidic amount provides many acidic sites, which can help to improve the efficiency for the conversion of cellulose into HMF.³⁴ Therefore, 185 µmol g⁻¹ of strong acid sites at 378 °C and 557 °C for PDVB-SO₃H, 264 µmol g⁻¹ of strong acid sites at 369 °C and 518 °C for PDVB-SS-SO₃H, and 237 μ mol g⁻¹ of super-strong acid sites at 604 °C and 706 °C for HC-PDVB-SS-SO₃H were effective to catalyze the conversion of cellulose into HMF. Furthermore, the fact that strong acid sites played a key factor for cellulose conversion was tested in our recent work.8 Thus, HC-PDVB-SS-SO₃H would possess predominant catalytic activity over PDVB-SO3H and PDVB-SS-SO₃H, owing to the number of strong acid sites. These results supported that HC-PDVB-SS-SO3H was selected in the further catalytic activity studies.

3.3 Conversion of cellulose to HMF

The experimental data of the correlation of three variables, such as catalyst dosage (m, mg), temperature (T, °C) and reaction time (t, h), were fitted using a low-order polynomial equation to evaluate the effect of each independent variable on the response. Moreover, in this work, the conversion efficiency was evaluated by the analysis of variance (ANOVA) with the HMF yield (Y, mol%) as the response, and the final obtained equation of HC-PDVB-SS-0-SO₃H in terms of the actual factors is expressed in eqn (2).

$$Y = -666.19 + 9.36T + 52.94t + 1.47m - 0.3Tt - 4.96$$

× 10⁻³Tm - 0.04tm - 0.03T² - 3.37t² - 6.34 × 10⁻³m₂ (2)

The 3D response surface and the 2D contour plots showing the effects of three variables for HC-PDVB-SS-SO₃H catalyst on HMF yield are displayed in Fig. 9. The interaction between the amount of catalyst and temperature on HMF yield under constant reaction time (1.75 h) are shown in Fig. 9a and b. With an increase in the amount of catalyst and temperature, it is obvious that HMF yield showed a trend of rapid increase in the beginning stages, and then reaching the maximum, and finally reduced with more catalyst and higher temperature used. The phenomenon may be attributed to the following reasons. First, the increasing reaction temperature and amount of catalyst reduced the viscosity of ionic liquids and increased contact area between catalyst and the reactants, which had the benefit to accelerate the degradation of cellulose.35 Second, the produced HMF covered the acid sites of catalysts, and the conversion of HMF into other tarry substances, such as insoluble humines



Fig. 8 NH₃-TPD curves of PDVB-SO₃H (a), PDVB-SS-SO₃H (b) and HC-PDVB-SS-SO₃H (c).



Fig. 9 Optimization of reaction conditions of the conversion of cellulose to HMF using HC-PDVB-SS-SO₃H as the catalyst through response surface methodology. The effects of (a) and (b) amount of catalyst and temperature for 1.75 h; (c) and (d) reaction time and amount of catalyst at 125 $^{\circ}$ C; (e) and (f) reaction time and temperature with 45 mg of HC-PDVB-SS-SO₃H.

and soluble polymers by the polymerization and crosspolymerization of HMF were enhanced with the further increasing reaction temperature and amount of catalyst.³⁶ In addition, Qu's groups also presented similar results.³⁷ Moreover, several researchers also reported the fact that the byproducts formic acid and levulinic acid could be examined by HLPC in this process.^{38,39} Interestingly, the same phenomenon was also observed in Fig. 9c and d, as well as in Fig. 9e and f, which indicate that the bidirectional interaction between variables, such as reaction time and amount of catalyst at 125 $^{\circ}$ C, reaction time and temperature with 45 mg catalyst, were also important terms in the production of HMF from cellulose. Moreover, the sequence of the three variables affecting HMF yield followed the order, temperature > reaction time > amount of catalyst, which was easily obtained according to the number of crosslinking of the contour plots with the coordinate axis of

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Fig. 9b, d and f, respectively. The optimal condition achieved by the response surface methodology was 0.10 g cellulose, 45 mg of catalyst, temperature of 125 °C, and reaction time of 1.75 h. The optimal HMF yield of 28.9% was closer to the experimental value of 29.2%, indicating that the predications were reasonable and credible.

In order to discuss the influence of the performance of materials on the conversion of cellulose into HMF, the optimal HMF yield of PDVB-SO₃H (22.3%) and PDVB-SS-SO₃H (25.2%) under the same conditions were obtained (50 mg of catalyst, 2.0 h of reaction time and 130 °C of reaction temperature) using the same analysis method, which are also listed in Table 2. It was clearly determined that HC-PDVB-SS-SO₃H obtained a higher HMF yield compared to the other two catalysts. BET specific surface and super-strong acid sites were considered to be responsible for the excellent performance of HC-PDVB-SS-SO₃H. First, higher BET specific surface area helped to increase contact frequency between reaction substrates and catalytic acid sites. Second, having more super-strong acid sites was more conducive to improve the catalytic effect of the conversion of cellulose to HMF than other types of acid sites. Moreover, the HMF yield of PDVB-SS-SO₃H was slightly higher compared to PDVB-SO₃H owing to the main advantages of BET specific surface area and total acidity. According to the above discussion about the performance of catalysts, it could be concluded that higher BET specific surface area and more super-strong acid sites of HC-PDVB-SS-SO₃H, as the remarkable effects, effectively facilitated the conversion of cellulose to HMF.

3.4 Regeneration of HC-PDVB-SS-SO₃H catalyst

The regeneration of catalyst was very important for the practical production of HMF, which was accorded with the demand of green and sustainable chemistry. Therefore, to evaluate the reusability of HC-PDVB-SS-SO₃H catalyst, recycling tests were conducted at the optimized reaction conditions. The results for the regeneration experiment are shown in Fig. 10. The solid acid catalysts HC-PDVB-SS-SO₃H were recovered by simple suction filtration using a Hirsch funnel with the mixture products diluted with deionized water after the end of the first reaction, washing them several times with a mixture of *n*-hexane and methanol, and drying at 30 °C for 24 h in a vacuum oven. Subsequently, recovered HC-PDVB-SS-SO₃H was used to catalyze the conversion of cellulose into HMF for four times, and the yields of HMF were 28.7%, 27.5%, 27.4%, and 26.5%, respectively. It was determined that the HMF yield slowly reduced. It was probably because the formation of by-product on the catalytic centers of HC-PDVB-SS-SO3H could not wash out into a mixture of n-hexane and methanol, which limited the accessibility of new reactant molecules to the sulfonic acid sites. However, the HC-PDVB-SS-SO₃H catalyst still had good activity after reusing it four times. Moreover, the FTIR spectra regenerated HC-PDVB-SS-SO₃H of was similar with HC-PDVB-SS-SO₃H, especially the intensity of the peaks of Si-O-Si and -SO₃H groups (Fig. 4), indicating that the HC-PDVB-SS-SO₃H catalyst possessed a rigid structure and



Fig. 10 Reusability of HC-PDVB-SS-SO₃H catalyst in the dehydration of cellulose into HMF in [EMIM]Cl under the optimized conditions: 125 °C, 45 mg of catalyst based on 0.10 g of cellulose, 1.75 h, [EMIM]Cl 2.0 g.

stable acidic active sites. The superior recyclability of HC-PDVB-SS-SO₃H occurs from their excellent chemical and mechanical stability of both acidic sites and polymer network, which were very important for their widely practical applications. These results, to some extent, suggested that the heterogeneous HC-PDVB-SS-SO₃H catalyst has the potential to be effectively recycled and reused for the dehydration reaction.

4. Conclusion

In this work, porous solid acid catalyst (HC-PDVB-SS-SO₃H) with high surface area was derived from pickering HIPEs template and a hypercrosslinking process. Then, the production of HMF from cellulose using HC-PDVB-SS-SO₃H as a catalyst in the presence of [EMIM]Cl was proved to be feasible, and obtained a yield of HMF at 29.2% for HC-PDVB-SS-SO₃H at the optimized conditions. Moreover, the fact that the BET specific surface area and super-strong acid site of catalyst are the key factors over the other three factors, including temperature, time and catalyst loading, was identified by ANOVA. This work was the continuation of the efforts to prepare a stable polymeric solid acid, and the results from this work could be valuable for future research towards the development of new reactors, especially their wide application for biomass and bioenergy production.

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