

Hierarchically Macro-/Mesoporous Polymer Foam as an Enhanced and Recyclable Catalyst System for the Sustainable Synthesis of 5-Hydroxymethylfurfural from Renewable Carbohydrates

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Renewable and abundant carbohydrates are being strongly focused upon as a green and sustainable alternative for the production of valuable chemicals and biofuels. In this study, we chemically integrated acid–base bifunctionalized mesoporous silica nanoparticles (MSNs-SO₃H-NH₂) and a macroporous polymer foam poly(HIPE) (PH) matrix that is derived from water-inoil (W/O) high internal phase emulsion (HIPE) templating. After the subsequent sulfonation process, a SPHs@MSNs-SO₃H-NH₂ catalyst with a hierarchical porous structure and bifunctional sites was prepared and used for the highly efficient synthesis of top value-added 5-hydroxymethylfurfural (HMF) from renewable cellulose in an ionic liquid (i.e., 1-ethyl-3-methylimidazolium chloride, [EMIM]Cl) based system. Evaluation of the catalytic activity revealed that the designed macropores were favorable for ready mass transfer, whereas the high surface area for active-site anchoring provided by the mesoporous structure was beneficial in enhancing the catalyst performance. A theoretical study also suggested that acidic and basic active sites synergistically work for the transformation reaction. Under the optimized conditions, a remarkably high HMF yield (44.5%) was obtained efficiently. Furthermore, the as-prepared catalyst was recycled in four consecutive cycles with a total loss of only 4.9% activity.

Introduction

Recently, the diminishing availability of traditional fossil resources and growing environmental problems have been the impetus behind burgeoning efforts to develop technologies that use renewable resources for the sustainable development of biofuels and platform chemicals. As the only sustainable source of organic carbon and a primary energy carrier, abundant biomass has evolved as the most promising alternative to provide valuable intermediates through a carbon-neutral way in the chemical industry.^[11] It is noticeable that the versatile and top value-added 5-hydroxymethylfurfural (HMF), which can be easily produced from renewable carbohydrates by the acid-catalyzed dehydration of hexoses, has received fruitful advancements in academia owing to its wide applications in the synthesis of fine chemicals,^[2] polymer precursors,^[3] fuels,^[4] and so forth. Nevertheless, the sustainable and large-scale production

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of HMF by current approaches has never been implemented commercially because the utilization of edible carbohydrates competes with the food supply.

Accordingly, employment of the most abundant organic compound of inedible cellulose for the production of HMF would be preferable.^[5] Moreover, the utilization of cellulose, present in lignocellulosic materials such as wood, straw, grass, municipal solid waste, and crop residues, does not compete with the food supply.^[6] In general, the transformation of cellulose into HMF involves multiple steps (i.e., hydrolysis, isomerization, and finally dehydration to HMF).^[7] Therefore, Qi et al. developed a two-step catalytic system including a strong acidic cation-exchange resin for cellulose hydrolysis and CrCl₃ for glucose degradation, and an excellent HMF yield was obtained.^[8] Compared with multiple reactions, a one-pot synthesis is an attractive methodology with respect to energy conservation and time-saving. To this end, intense research activity should focus on exploring efficient catalytic systems for the one-pot synthesis of HMF directly from renewable cellulose.^[9]

During the past few years, different types of solid acids have been considered as good candidates for biomass transformation because they are generally associated with a lower production of waste, the use of fewer toxic reagents, and easier recycling over conventional liquid acids.^[10] In particular, fineparticle-based catalysts with very small size and mesoporous structure have attracted a surge of interest owing to their high surface area. For example, a mesoporous carbonaceous solid



(CS) catalyst was successfully synthesized by Wang's group, and the catalyst was proved to have high activity for the synthesis of HMF from fructose.^[11] Mazzotta et al. prepared mesoporous sulfonated carbonaceous TiO₂ and the obtained catalyst also showed good catalytic activity for the dehydration of glucose to HMF.^[12] However, it was difficult for the large polymer molecules of cellulose to diffuse deeply inside the mesoporous solid through the small pore diameters, which limited the accessibility of active sites and negated the merits of the high surface area.^[13] In addition, it was difficult to maintain the small particle morphology in the reaction process, and the separation of catalysts from the reaction mixture was also inconvenient. These shortcomings strongly hinder the practical application of mesoporous materials in the field of cellulose transformation. More recently, hierarchical porous materials with a bimodal macro-/mesoporous structure have been very attractive in a wide range of catalytic applications.^[14] Different pore sizes integrated in one body was efficient for cellulose transformation reactions, in which the macropores ensure the rapid transport of the reactant and the mesopores provide a high surface area for the reaction to take place.^[15] The main shortcomings of mesoporous catalysts (i.e., limited accessibility of cellulose with active sites) could also be overcome by using hierarchical porous catalysts. Moreover, Takagaki et al.^[16] and Peng et al.^[17] made a significant contribution to improving the catalytic performance in the one-pot synthesis of HMF directly from cellulose. In their study, an acid-base bifunctional catalyst was successfully designed and firstly applied to the cellulose transformation with high HMF yields generated. It has been demonstrated that a catalytic system that contains both acidic and basic active sites is more beneficial for HMF production from cellulose than acidic catalysts alone, as basic catalysts show advantageous properties for the isomerization process during the cellulose transformation reaction.^[18] Consequently, exploring simple methods for the fabrication of catalysts with hierarchically macro-/mesoporous structures and acid-base bifunctional active sites would be helpful for one-pot celluloseto-HMF conversion.

Recently, high internal phase emulsion (HIPE) templating, a simple and versatile tool, has drawn widespread attention in a wide range of preparations of cellular macroporous materials.^[19] HIPEs are known as emulsions with an internal phase (volume fraction $>\!74\,\%$) and external phase. Poly(HIPEs) with low density and open-cell structure are usually synthesized by polymerizing the monomers in the external phase of HIPEs and removing the internal phase. Moreover, the pore structure and interconnectivity of the poly(HIPEs) can be easily tailored by varying parameters in the HIPE template.^[20] By using this method, macroporous polymerized solid acid with an opencell structure, interconnecting pores, and strong acidity was synthesized in our previous study.[21] Owing to its porosity, high permeability, and stability in the reaction mixture, the catalyst exhibited comparable activity with a homogeneous catalyst of equal acidity in one-pot cellulose-to-HMF conversion, and can be reused at least five times without significant loss of catalytic activity.

Herein, we chemically integrated acid–base bifunctionalized mesoporous silica nanoparticles (MSNs-SO₃H-NH₂) and a macroporous polymer foam poly(HIPE) (PH) matrix that was derived from water-in-oil (W/O) HIPE templating. After a subsequent sulfonation process, a SPHs@MSNs-SO₃H-NH₂ catalyst with hierarchical porous structure and acid–base bifunctional sites was successfully prepared. As illustrated in Scheme 1, the as-pre-



Scheme 1. Catalyst behavior in one-pot cellulose-to-HMF conversion.

pared catalyst was employed for the highly efficient synthesis of HMF from renewable cellulose involving sequential catalytic processes in an ionic liquid [EMIM]Cl-based system. The catalytic activity was evaluated in detail, and the regeneration performance of the catalyst was also investigated. This study is part of the continued effort to fabricate and apply multifunctional catalysts in the one-pot conversion of cellulose to HMF in excellent yield.

Results and Discussion

Morphology and hierarchical porous structure of the samples

In this study, PHs with tailored pore sizes and interconnectivity were fabricated by tailoring the volume fraction of the internal phase from 75 to 90%, as described in the Experiment Section. Figure 1A–D exhibit scanning electron microscopy (SEM) images of PHs1, PHs2, PHs3, and PHs4, respectively. SEM images reveal that an open cellular structure exists in all cases, and the voids are highly interconnected by means of spherical pore throats. However, in the cases of PHs1 and PHs2, a clear bimodal cavity-like structure is observed in Figure 1A and B. The observed bimodal cavity-size distribution was most probably caused as a consequence of the reduced emulsion stability and subsequent occurrence of coalescence before the gel point of polymerization.^[22] It has been proven that increasing the volume fraction of the internal phase leads to a highly viscous emulsion, and the emulsion stability should be increased, which results in an increasing number of smaller droplets, and hence increased droplet contact.^[23] Since poly(HIPE) is a replica of the emulsion templating at the gel point of the polymerization, it was not surprising that on further increasing the volume fraction of the internal phase to 85 and 90%, microcellular foam-like PHs3 and PHs4 with relatively uniform pore size



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Figure 1. SEM images of poly(HIPE) synthesized from emulsion templates containing internal phases of (A) 75, (B) 80, (C) 85 (inset: magnified SEM image), and (D) 90 vol %.

distribution were obtained (see inset in Figure 1C). Moreover, it can be concluded that the average diameter of the large void (*D*) and pore throats (*d*) decreased significantly, whereas the degree of interconnectivity was dramatically enhanced on increasing the volume fraction of the internal phase as shown in Table 1.

Table 1.	Composition	of	emulsion	templates	and	the	parameters	of	the
resulting	g poly(HIPE).								

Entry	HIPE	Vol. fract. [%] ^[a]	Surf. [wt %] ^[b]	Poly(HIPE) ^[c]	D [μm] ^[d]	<i>d</i> [μm] ^[e]	/ [%] ^[f]
1	Hs1	75	1.0	PHs1	29.3	2.8	9.1
2	Hs2	80	1.0	PHs2	21.3	3.2	11.3
3	Hs3	85	1.0	PHs3	14.7	4.3	34.2
4	Hs4	90	1.0	PHs4	14.2	4.0	28.6

[a] Volume fraction of the internal phase in the emulsion templates. [b] Surfactant amount with respect to the continuous phase. [c] Relevant poly(HIPE) that was prepared by curing the HIPE for 24 h at 65 °C. [d] Average void diameter of the poly(HIPE) estimated from the SEM images. [e] Average interconnecting pore diameter directly measured from the SEM images. [f] Interconnectivity of as-prepared poly(HIPE) calculated by using $n \times (d/D)^2 \times 100$, in which *n* is the average number of interconnecting pores per void.

To strengthen the catalytic activity of the final hierarchical porous catalysts, MSNs and their acid-functionalized MSNs-SO₃H and acid-base bifunctionalized MSNs-SO₃H-NH₂ were fabricated. Figure 2A–C shows the corresponding transmission electron microscopy (TEM) images of MSNs, MSNs-SO₃H, and MSNs-SO₃H-NH₂, respectively. Clearly, MSNs with a diameter of (100 \pm 8) nm and random pore structure were synthesized by using the ammonia-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS) in an aqueous solution (seen inset in Figure 2A). After the functionalization process of MSNs with organosilane, the diameter increased to (130 \pm 5) nm with MSNs-SO₃H-NH₂ (Figure 2C), and (150 \pm 5) nm with MSNs-SO₃H-NH₂ (Figure 2C),



Figure 2. TEM images of (A) MSNs (inset: magnified TEM image of the corresponding MSNs, scale bar: 20 nm), (B) MSNs-SO₃H, and (C) MSNs-SO₃H-NH₂; (D) SEM image of PHs3@MSNs-SO₃H-NH₂.

which indicates the successful grafting of 3-(mercaptopropyl)trimethoxysilane (MPTMS) and (aminopropyl)trimethoxysilane (APTMS) onto the surface of MSNs. It should also be noted that particle agglomeration appears in Figure 2C, which was attributed to the grafted hydrophilic organosilane (i.e., MPTMS and APTMS) on the MSNs surface. MSNs-NH₂ with only basic active sites and an average diameter at (125 ± 5) nm was also obtained by us as shown in Figure S3 in the Supporting Information. In practical applications, the introduction of smaller pores into a macroporous structure is important. This is because the presence of macropores allows the mass transfer of the bulk of the substances like liquids and gases, whereas the smaller pores create a large internal surface area that greatly enhances the catalytic properties.^[24] In this study, PHs3 was employed as a matrix to integrate with acid-base bifunctional mesoporous MSNs-SO₃H-NH₂. As shown in Figure 2D, the synthesized composite is composed of silica particles and PHs matrixes, thereby establishing that the MSNs-SO3H-NH2 was successfully introduced onto the framework of macroporous matrixes. In addition, SNs with a diameter of (124 ± 6) nm, acidbase bifunctionalized SNs-SO_3H-NH_2 with a diameter of (164 \pm 6) nm, and PHs3@SNs-SO₃H-NH₂ composite were also successfully obtained (Figure S4 in the Supporting Information).

FTIR spectra of the MSNs, MSNs-NH₂, MSNs-SO₃H-NH₂, PHs3 matrixes, and SPHs3@MSNs-SO₃H-NH₂ composite are displayed in Figure 3A. On comparing Figure 3A a and c, the existence of MPTMS and 3-aminopropyltriethoxysilane (APTES) on the surface of MSNs-SO₃H-NH₂ can be established. The appearance of the vibration peaks assigned to Si–OH around 955 cm⁻¹ and –OH at approximately 3200–3500 cm⁻¹ in the FTIR spectrum of MSNs can be observed (Figure 3A a), whereas these characteristic peaks disappear in Figure 3A c owing to the chemical reaction between the Si–OH groups of MSNs and alkoxy groups of organosilanes. Thus, the Si–OH bonds of the MSNs surface were changed into new Si-O-Si bonds. The chemical structure of the PHs3 macroporous monolith before and after





Figure 3. (A) FTIR spectra of (a) MSNs, (b) MSNs-NH₂, (c) MSNs-SO₃H-NH₂, (d) PHs3 matrix, and (e) SPHs3@MSNs-SO₃H-NH₂ composite; (B) elemental contents of MSNs-SO₃H-NH₂ and SPHs3@MSNs-SO₃H-NH₂ composite.

introduction of MSNs-SO₃H-NH₂ was compared with that of Figure 3A d and e. It can be clearly seen that the characteristic peak of epoxy groups at 910 cm⁻¹ disappeared after grafting MSNs-SO₃H-NH₂, which was mainly attributed to the chemical reaction of $-NH_2$ with epoxy groups. These results also confirmed that MSNs-SO₃H-NH₂ was chemically integrated onto the PHs3 matrix rather than mere physical integration. After the sulfonation process, a clear new peak around 570 cm⁻¹ associated with the C–S bond was clearly observed in Figure 3A e, which indicates more sulfonic groups have been successfully incorporated.^[25] Results of elemental analysis of the MSNs-SO₃H-NH₂ and SPHs3@MSNs-SO₃H-NH₂ composite are shown in Figure 3B. Clearly, both of the samples possessed the elements C, H, S, and N, which suggests the successful chemical combination of MSNs-SO₃H-NH₂ with the PHs3 matrix.

The nitrogen adsorption–desorption isotherms and the pore-size distribution curves of MSNs (A, a), MSNs-SO₃H (B, b), MSNs-SO₃H-NH₂ (C, c), and SPHs3@MSNs-SO₃H-NH₂ (D, d) are displayed in Figure 4. Clearly, both of the samples exhibit typical type IV isotherms with a step capillary condensation in the relative pressure range of 0.1–0.9, which confirms the mesoporosity in these samples.^[26] Moreover, the porosity properties of MSNs, MSNs-SO₃H, MSNs-SO₃H-NH₂, and SPHs3@MSNs-SO₃H-



Figure 4. Top: Nitrogen adsorption–desorption isotherms of (A) MSNs, (B) MSNs-SO₃H, (C) MSNs-SO₃H-NH₂, and (D) SPHs3@MSNs-SO₃H-NH₂. Bottom: Pore-size distribution curves of (a) MSNs, (b) MSNs-SO₃H, (c) MSNs-SO₃H-NH₂, and (d) SPHs3@MSNs-SO₃H-NH₂.

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Table 2. The porosity properties of the samples.							
Entry	Samples	S_{BET} [cm ² g ⁻¹] ^[a]	D _{BJH} [nm] ^[b]	V _t [cm ³ g ⁻¹] ^[c]			
1	MSNs	195.5	8.0	0.21			
2	MSNs-SO ₃ H	141.8	14.4	0.14			
3	MSNs-SO ₃ H-NH ₂	97.1	22.8	0.10			
4	SPHs3	0.06	-	-			
5	$SPHs3@MSNs-SO_3H-NH_2$	45.4	22.6	0.09			
[a] BET specific surface area. [b] Pore diameter calculated from the desorp- tion branch of the corresponding nitrogen isotherms, by applying the							

tion branch of the corresponding nitrogen isotherms, by applying the BJH method. [c] Total pore volume determined at the relative pressure of 0.99.

NH₂ are listed in Table 2. Clearly, the Brunauer-Emmett-Teller surface area (195.5 cm^2g^{-1}) and pore volume (BFT) (0.21 cm³g⁻¹) of MSNs are higher than those of MSNs-SO₃H $(141.8\ cm^2g^{-1},\quad 0.14\ cm^3g^{-1}),\quad MSNs\text{-}SO_3H\text{-}NH_2\quad (97.1\ cm^2g^{-1},$ 0.10 cm³ g⁻¹), and SPHs3@MSNs-SO₃H-NH₂ $(45.4 \text{ cm}^2 \text{g}^{-1})$ 0.09 cm³ g⁻¹), respectively. Nevertheless, the Barrett–Joyner–Halenda (BJH) pore diameter (8.0 nm) of MSNs is lower than that of MSNs-SO₃H (14.4 nm) and MSNs-SO₃H-NH₂ (22.8 nm). These results were mainly attributed to the introduction of organosilane that blocked the mesopores of MSNs and particle agglomeration, thereby resulting in larger pores in MSNs-SO3H and MSNs-SO₃H-NH₂. After the integration of MSNs-SO₃H-NH₂ and the PHs3 matrix, BET surface area of the final SPHs3@MSNs- SO_3H-NH_2 catalyst sharply increased from 0.06 to 45.4 cm³g⁻¹, with a pore volume of 0.09 cm³g⁻¹ and mesopores of approximately 22.6 nm in diameter. The as-prepared SPHs3@MSNs-SO₃H-NH₂ catalyst with such a hierarchically macro-/mesoporous structure was particularly intriguing in cellulose-to-HMF conversion, in which the interconnected macropores would allow ready mass transfer, and the mesopores along the macroporous walls might have a specific large surface area and greatly enhance the catalytic activities.

Chemical composition of the catalysts

The SEM-equipped energy-dispersive X-ray spectroscopy (EDS) analyses of MSNs-SO₃H-NH₂ and SPHs3@MSNs-SO₃H-NH₂ are given in Figure 5. Peaks corresponding to C, N, and S are apparent, which suggests the successful introduction of MPTMS and APTES onto the surface of MSNs, in accord with the results of elemental analysis. After the integration of the MSNs-SO₃H-NH₂ and PHs3 matrix, and the subsequent sulfonation process, the final catalyst of SPHs3@MSNs-SO₃H-NH₂ gives a more obvious S peak as shown in Figure 5B, which was attributed to more sulfonic groups being successfully introduced. As previously reported, the strengthened acidic active sites in SPHs3@MSNs-SO₃H-NH₂ should have beneficial properties in one-pot cellulose-to-HMF conversion due to the catalyst acidity playing a key role in the cellulose hydrolysis and monosaccharide dehydration processes.^[27]

The condensed structural formula of SPHs3 (Figure 6A) was determined by using ¹³C cross-polarization (CP)/magic-angle spinning (MAS) NMR spectroscopy as shown in Figure 6D. The







Figure 5. EDS of (A) MSNs-SO₃H-NH₂ and (B) SPHs3@MSNs-SO₃H-NH₂.



Figure 6. Top: The condensed structural formulas of (A) SPHs3, (B) MSNs-NH₂, and (C) MSNs-SO₃H; (D) ¹³C solid-state NMR spectra of SPHs3 and SPHs3@MSNs-NH₂-SO₃H; (E) NMR spectra curve-fitting result of signals C7,8,9,10 with catalyst SPHs3@MSNs-NH₂-SO₃H.

signal detected at $\delta = 143.1$ ppm corresponds to carbon atoms bonded to sulfonic acid groups. And the as-prepared SPHs3@MSNs-SO₃H-NH₂ composite reveals almost the same signals in the ¹³C NMR spectra except for two new signals as shown in Figure 6E. First, the signal detected at $\delta = 44.9$ ppm is assigned to carbon atoms of C–NH₂ (C9 in Figure 6B), which indicates the appearance of other acid functionalities.^[28] Second, another signal, detected at $\delta = 55.0$ ppm in the ¹³C NMR spectrum, was assigned to the carbon atoms of C– SO₃H (C10 in Figure 6C), thereby establishing the presence of the acid functionality.^[29] These observations confirmed the successful synthesis of the acid–base bifunctional and hierarchically meso-/macroporous SPHs3@MSNs-SO₃H-NH₂ catalyst, which was consistent with the results obtained from FTIR spectroscopic analysis.

The chemical composition of MSNs-SO₃H-NH₂ and SPHs3@MSNs-SO₃H-NH₂ and their chemical status were analyzed by X-ray photoelectron spectroscopy (XPS), and the results are shown in Figure 7. The survey spectrum gave signals mainly associated with C1s, O1s, N1s, S2p, and Si2p species for both MSNs-SO₃H-NH₂ and SPHs3@MSNs-SO₃H-NH₂, which indicated that the catalysts were composed of C, O, N, S, and Si elements. The high-resolution XPS spectra of the C 1s region of MSNs-SO₃H-NH₂ and SPHs3@MSNs-SO₃H-NH₂ are shown in Figure 7B, C. Both of the two samples possess characteristic peaks of C–C (284.6 eV), C=C (285.0 eV), C=O, and C–N



Figure 7. XPS survey spectrum in the binding-energy range of 0–1000 eV (A) and high-resolution spectra of C1s (B, C), N1s (D), S2p (E), and O1s (F) of $MSNs-SO_3H-NH_2$ and $SPHs3@MSNs-SO_3H-NH_2$.

(285.4 eV), which were mainly attributed to the successful introduction of organosilane onto the surface of MSNs and integration of MSNs-SO₃H-NH₂ and the PHs3 matrix. Notably, as shown in Figure 7C for the partial enlarged view of C1s with SPHs3@MSNs-SO₃H-NH₂ catalyst, a new peak at 287.8 eV was observed and assigned to the C=O group, derived from the polymerized glycidyl methacrylate monomer in the PHs3 matrix. As shown in Figure 7D, the peak at 400.9 eV corresponds to N1s, which suggests that basic amino groups existed in MSNs-SO₃H-NH₂. However, the signal of N 1s in SPHs3@MSNs-SO₃H-NH₂ shifts from 400.9 to 400.58 eV, which is ascribed to the chemical reaction of -NH₂ with epoxy groups. Additionally, the S2p spectra consisting of two peaks located at 167.8 and 152.8 eV, which correspond to S2p_{1/2} and S2p_{3/2} in Figure 7E, respectively, establish the presence of sulfonic groups in MSNs-SO₃H-NH₂ due to the binding energy of S2p being sensitive to the acidic strength.^[30] High-resolution XPS spectra of O1s for MSNs-SO3H-NH2 and SPHs3@MSNs-SO3H-NH₂ was located at a binding energy of 531.8 eV (Figure 7F).

Acidic and basic properties of the catalysts

Temperature-programmed FTIR spectroscopy using pyridine as a Lewis base is one of the most important analytical tools for characterizing the acidic properties of catalysts. Figure 8 presents the pyridine-desorption FTIR spectra of MSNs-SO₃H-NH₂, SPHs3, and SPHs3@ MSNs-SO₃H-NH₂ at 25, 50, 150, and 250 °C,



Figure 8. Pyridine-desorption FTIR spectra of (A) MSNs-SO₃H-NH₂, (B) SPHs3, and (C) SPHs3@MSNs-SO₃H-NH₂ at (a) 25, (b) 50, (c) 150, and (d) 250 $^{\circ}$ C.

respectively. A band at 1450 cm⁻¹, which is assignable to absorbed pyridine at the Brønsted acidic sites, is observed for all three catalysts. Upon increasing the temperature to 250 °C, SPHs3 and SPHs3@MSNs-SO₃H-NH₂ exhibit a decrease in intensity of this band caused by desorption of surface-bound pyridine from the catalyst surface. This behavior indicates the presence of weakly chemisorbed pyridine, which was hydrogenbonded to the Brønsted acid sites of the $-SO_3H$ groups.^[31]

In addition to the pyridine IR spectroscopy results, which show evidence of Brønsted acid sites in the catalyst, the catalyst acid and alkaline densities were evaluated by temperatureprogrammed desorption (TPD) of NH₃ and CO₂. Ammonia and carbon dioxide desorption experiments were performed at a linear heating rate of 10°C per minute up to a temperature of 400 °C as the thermogravimetric analysis (TGA) of the catalyst indicated a significant mass loss at higher temperature (Figure S5 in the Supporting Information). Figure 9 lists the typical NH₃-TPD and CO₂-TPD curves of MSNs-SO₃H-NH₂ and SPHs3@MSNs-SO₃H-NH₂, respectively. Desorption peaks are observed at various temperatures. Among the desorbed NH₃ or CO_2 molecules, those appearing at ≤ 150 °C correspond to the physically adsorbed NH₃ or CO₂, whereas those appearing at higher temperatures correspond to molecules released from acidic or basic sites.^[32] Each desorption peak (except for those appearing at < 150 °C) in Figure 8 was integrated to measure the corresponding acid or alkaline density as described in the

Experimental Section. Table 3 shows the corresponding acidic and basic features of the as-prepared catalysts in detail. It is evident that after the functionalization of MSNs with MPTMS and APTES, the obtained MSNs- SO_3H-NH_2 possessed a total acidity of 0.23 mmol g⁻¹ and basicity of 1.06 mmol g⁻¹. Moreover, the final catalyst of



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Figure 9. NH₃-TPD curves of (A) MSNs-SO₃H-NH₂ and (B) SPHs3@MSNs-SO₃H-NH₂; CO₂-TPD curves of (C) MSNs-SO₃H-NH₂ and (D) SPHs3@MSNs-SO₃H-NH₂.

SPHs3@MSNs-SO₃H-NH₂ had a higher total acidity of 3.10 mmol g⁻¹ and basicity of 0.45 mmol g⁻¹, respectively. Catalyst SPHs3@SNs-SO₃H-NH₂ was calculated to possess a total acidity of 3.0 mmol g⁻¹ and basicity of 0.41 mmol g⁻¹, which was comparable to that of PHs3@MSNs-SO₃H-NH₂ (Figure S6 in the Supporting Information).

Conversion of cellulose to HMF

The performances of catalysts SPHs1, SPHs2, SPHs3, and SPHs4 were determined by evaluating the HMF yields from cellulose in a one-pot reaction. All reaction steps were repeated three times as depicted in the Experimental Section, and the average yield of HMF was calculated. First, SPHs3 (40 mg) was used to degrade cellulose to HMF at temperatures ranging from 110 to 150 $^\circ\text{C}.$ Reaction times ranging from 10 to 60 minutes were used to optimize the reaction conditions and to maximize the HMF yield. As shown in Figure 10A, the HMF yields gradually improve as the temperature increases from 110 to 150°C within the first 10 minutes. The highest HMF yield of 32.4% was obtained at 120 °C within 10 minutes. This excellent catalytic performance was mainly attributed to the high porosity and permeability of catalyst SPHs3. However, when the reaction time was further extended to 60 minutes, the HMF yields at all temperatures decreased. Furthermore, it was evident that the highest HMF yield of 37.5% was obtained at 120°C and

Table 3.	Table 3. The acidic and basic features of as-prepared catalysts.								
Entry	Sample	S content $[mmol g^{-1}]^{[a]}$	Acidity $[mmol g^{-1}]^{[b]}$	N content $[mmol g^{-1}]^{[a]}$	Basicity [mmol g ⁻¹] ^[c]				
1	MSNs-SO₃H	0.36	0.45	-	-				
2	MSNs-SO ₃ H-NH ₂	0.18	0.23	1.04	1.06				
3	SPHs3	3.04	2.86	-	-				
4	SPHs3@MSNs-SO ₃ H-NH ₂	3.12	3.10	0.49	0.45				
[a] Calculated by elemental analysis. [b] Measured by using the NH_3 -TPD method. [c] Measured by using the CO_2 -TPD method.									



Figure 10. (A) Effect of reaction time at different temperatures on HMF yields from cellulose catalyzed by SPHs3, and (B) HMF yields obtained with varied catalyst loading.

30 minutes. This observation suggested that an increase in reaction time or temperature may result in the formation of some undesired byproducts such as soluble polymers and insoluble humins.^[33] Although these byproducts were difficult to indentify using the present techniques, their generation was confirmed by the color changes of the reaction mixture (Figure S7 in the Supporting Information), which coincided with the results of Wang's study.^[11] Therefore, subsequent experiments were performed over 120 °C and 30 minutes.

Figure 10B shows the optimized amount of catalysts SPHs1 through SPHs4 in terms of the maximum yield of HMF. The catalyst loading amounts varied from 10 to 50 mg, while the other reaction parameters were constant: T=120 °C, t=30 minutes. The results suggest that higher interconnectivity led to better catalytic performance. For instance, SPHs3 produced the greatest HMF yield of 37.5% with the least amount of catalyst (40 mg) owing to its high interconnectivity. The relative poor catalytic performance of SPHs1 and SPHs2 was caused primarily by their broad pore-size distribution.^[34] Therefore, PHs3 was employed as the matrix to integrate acid–base bifunctional mesoporous MSNs-SO₃H-NH₂.

Cellulose was used directly as a reactant in the cellulose-to-HMF conversion carried out in the ionic liquid (IL)-based system in the presence of MSNs-SO₃H-NH₂ catalyst. Figure 11A reveals the influence of the reaction time at different temperatures on HMF yields from cellulose catalyzed by MSNs-SO₃H-NH₂. The same trend was seen with catalyst SPHs3, and HMF yields gradually improved as the temperature increased from 110 to 140 °C within the first hour. However, as the time was further extended to 60 minutes, the HMF yields at all temperatures decreased owing to the formation of byproducts. The highest HMF yield with 31.2% was obtained at 120 °C and two hours. The optimized reaction temperature with MSNs-SO₃H-NH₂ was longer than that of macroporous SPHs3, which was mainly attributed to the lower permeability of the mesoporous structure.

Figure 11B shows the optimal catalyst amounts of acid-, base-, acid-base-functionalized, or unmodified MSNs for the maximum yields of HMF. The catalyst loading amounts varied from 10–50 mg, while the other reaction parameters were constant: T = 120 °C, t = 2.0 h. Clearly, the acid-base bifunctionalized MSNs-SO₃H-NH₂ catalyst gave a higher HMF yield at 31.2% than that obtained with acidic, basic, or blank MSNs catalysts, respectively. The enhanced HMF yield (31.2%) of MSNs-

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Figure 11. (A) Effect of reaction time at different temperature on HMF yields from cellulose catalyzed by $MSNs-SO_3H-NH_{2r}$ and (B) HMF yields obtained with varied catalyst loading.

SO₃H-NH₂ could be mainly attributed to the cooperative catalysis of both the acid and base functional groups in the catalyst.

Until now, the process of cellulose-to-HMF conversion has been thought to consist of four main stages, cellobiose-to-oligomer dissolution, oligomer-to-glucose depolymerization, glucose-to-fructose isomerization, and fructose-to-HMF dehydration.^[7] Cellulose, glucose, and fructose were adopted as substrates to directly assess the effects of the catalyst acid and base strengths on HMF yields in different reaction systems. Reports in the literature suggested that introduction of dimethyl sulfoxide (DMSO) into aqueous solution as a cosolvent can significantly increase the HMF yield in carbohydrate conversion.[35] Thus, DMSO/H₂O (2.0 mL, 1:1 v/v) was employed as the solvent with glucose or fructose as the substrate, while the other reaction parameters were held constant ($T = 120 \degree C$, t = 30 minutes, catalyst amount = 40 mg). It is evident from Figure 12A that the HMF yields and fructose conversion are greatly promoted in the presence of SPHs3, compared with the catalytic system containing no catalyst. However, a comparable HMF yield of 20.6% and fructose conversion percentage of 35.3% obtained in the blank catalytic system were attributed to the facile conversion of fructose to HMF in the DMSO/H₂O system at high temperature. Other groups have reported the same observation.^[17] Clearly, the HMF yield and selectivity obtained in the presence of acid-base bifunctional SPHs3@MSNs-SO₃H-NH₂ (88.0% HMF yield and 88.8% HMF selectivity) and acid SPHs3 (85.1% HMF yield and 86.7% HMF selectivity) were similar to each other. These results indicated that an acid catalyst was necessary for the dehydration of fructose to produce HMF and the presence of base made no sense in promoting HMF yield and selectivity.

The yields of HMF converted from glucose in the presence of acid–base bifunctional SPHs3@MSNs-SO₃H-NH₂ and acid SPHs3 catalysts are shown in Figure 12B. It is clearly seen that the cases with SPHs3@MSNs-SO₃H-NH₂ catalysts exhibited the highest HMF yield (66.9%) and HMF selectivity (72.3%), in contrast to those of SPHs3 (HMF yield 51.4% and selectivity 62.2%). The conversion of glucose to HMF involves two steps: glucose-to-fructose isomerization and fructose-to-HMF dehydration. From the results of fructose-to-HMF, we have confirmed that HMF can be easily converted from fructose in our reaction system in the presence of acid catalysts. Therefore, the improvement of SPHs3@MSNs-SO₃H-NH₂ catalytic performance can be explained by the existence of basic active





Figure 12. HMF yield, substrate conversion, and HMF selectivity with catalysts SPHs3 and SPHs3@MSNs-SO₃H-NH₂ in (A) one-pot fructose-to-HMF, (B) glucose-to-HMF, (C) fructose-to-HMF transformation.

sites, which are beneficial for the isomerization of glucose to fructose. $\ensuremath{^{[18]}}$

Previous study on fructose-to-HMF and glucose-to-HMF conversions confirmed that acidic active sites play an important role in the dehydration of fructose to HMF and that basic active sites enhance the isomerization of glucose to fructose. Acid catalysts can facilitate the oligomer-to-glucose depolymerization step in the cellulose-to-HMF process.[36] Therefore, SPHs3@MSNs-SO₃H-NH₂ with both acidic and basic active sites was more beneficial for HMF production from cellulose (HMF yield of 44.5% and HMF selectivity of 49.6%) than acidic catalyst SPHs3 alone, as shown in Figure 12C. Notably, SPHs3@SNs-SO₃H-NH₂ with a macroporous structure produced HMF in a yield of 40.8% from cellulose under the optimized conditions, lower than that of SPHs3@MSNs-SO3H-NH2, thereby establishing that the designed hierarchically macro-/mesoporous structure played a key role in improving the HMF yield. In a control experiment, an IL-based reaction system without catalyst produced an HMF yield of only 1.2%, which indicated the high catalytic performance of the as-prepared hierarchically macro-/mesoporous SPHs3@MSNs-SO₃H-NH₂ catalyst.

Recyclability of the catalysts

To make an evaluation of the catalyst recyclability, the cellulose-to-HMF conversion was studied over four cycles using SPHs3@MSNs-SO₃H-NH₂. All reaction conditions were the same as those of the fresh catalyst experiments mentioned in this study. Figure 13A shows that the mole yields of HMF remained at about 39.6%, which was a value comparable to that of the fresh catalyst, until the fourth run. No significant decrease in HMF yield was observed till the fourth run, which means that the immobilized $-SO_3H$ and $-NH_2$ functional groups were not leached extensively during the process. SEM images of reused SPHs3@MSNs-SO₃H-NH₂ after four runs (Figure 13B) reveals that catalysts with a microcellular foamlike structure were well

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Figure 13. (A) Recyclability of SPHs3@MSNs-SO₃H-NH₂ in the conversion of cellulose-to-HMF; (B) SEM images of reused SPHs3@MSNs-SO₃H-NH₂ after five runs; (C) XPS spectrum of SPHs3@MSNs-SO₃H-NH₂ after regeneration, and (D) elemental analysis of reused SPHs3@MSNs-SO₃H-NH₂ after five runs (inset: the acidity and basicity of reused SPHs3@MSNs-SO₃H-NH₂ calculated by elemental analysis).

maintained during the catalytic process. The superior recyclability of SPHs3@MSNs-SO₃H-NH₂ was the result of the superior thermal stability of its acidic sites and polymer network, which is an important property in practical applications. The above results suggest that, to some extent, the heterogeneous catalysts have great potential to be effectively separated and reused for dehydration reactions.

To establish the structural characteristics of the recycled catalyst, an XPS spectrum of SPHs3@MSNs-SO3H-NH2 that had been used for four cycles is recorded as shown in Figure 13C. Compared with the XPS spectrum of the fresh catalyst shown in Figure 7A, strong C 1s, O 1s, N 1s, S 2p, and Si 2p signals are observed, which indicates the superior chemical stability of asprepared SPHs3@MSNs-SO₃H-NH₂ during the repeated catalytic process. Elemental analysis for the catalyst after the fourth run shows that the S content decreased by 0.42% (Figure 13D). The acidity and basicity remained at 3.09 and 0.37 mmol g^{-1} , respectively. Results of the inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurements demonstrate that the sulfur concentration in the final products after the catalyst SPHs3@MSNs-SO₃H-NH₂ fifth run with was 0.02 mg mL^{-1} , which resulted from the leaching of $-SO_3H$ groups.

Conclusion

A hierarchically macro-/mesoporous SPHs@MSNs-SO₃H-NH₂ catalyst containing both acidic and basic sites has been successfully synthesized through the chemical combination of MSNs-SO₃H-NH₂ with macroporous PHs derived from water-inoil (W/O) HIPE templating, followed by a sulfonation process. The newly developed catalyst was used for the sustainable synthesis of HMF from renewable cellulose in an IL-based solvent system, and an enhanced HMF yield of 44.5% was obtained under optimized conditions. Moreover, the as-prepared



catalyst was also effective for the conversion of glucose and fructose to HMF in a DMSO/H₂O system, which enabled maximum HMF yields of 66.9 and 88.0%, respectively. The enhanced catalytic activity toward one-pot carbohydrate conversion for HMF synthesis was attributed to the designed hierarchically macro-/mesoporous structure and acid–base bifunctions. This study represents a continuation of efforts to make stable polymeric solid acids and provides results that will be valuable for future research directed toward the development of new reactors and their application in biomass conversion and bioenergy.

Experimental Section

Chemicals and reagents

Divinyl benzene (DVB), glycidyl methacrylate (GMA), azodiisobutyronitrile (AlBN), tetraethyl orthosilicate (TEOS, 98%), 3-(mercaptopropyl)trimethoxysilane (MPTMS, 99%), 3-aminopropyltriethoxysilane (APTES, 99%), hexadecyltrimethyl ammonium bromide (CTAB, 99%), dichloromethane (CH₂Cl₂), diethyl ether, *N*,*N*-dimethylformamide (DMF), pure HMF, and 1-ethyl-3-methyl imidazolium chloride ([EMIM]Cl) were purchased from Aladdin (Shanghai, China). Hypermer 2296 was kindly supplied by Foshan Excel Chemical Co., Ltd. (Fujian, China). Deionized water (DI, 18.2 mLcm⁻¹) was obtained through a Milli-Q water-purification system. All other chemicals and solvents were of reagent grade or better, and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Preparation of macroporous poly(HIPE) (PH) matrixes

As shown in Scheme 2, DVB (3.0 mL), GMA (1.0 mL), AIBN (0.05 g), and Hypermer 2296 (0.05 g) were dissolved in toluene (1.0 mL) in a round-bottomed flask with gentle stirring to form a continuous phase. After the dropwise addition of DI water (28.33 mL) as the dispersing phase, a stable W/O HIPE was obtained (Figure S1 in the Supporting Information). The obtained HIPE was then transferred to a sealed glass mold, and polymerized in a 50 °C oven for 24 h. Thereafter, the polymerized monolith was removed from the molds, dried in a vacuum at 50 °C for 24 h, and extracted in Soxhlet apparatus with acetone to remove any impurities. Finally, the resultant polymer foams were dried to a constant weight in a vacuum at 50 °C. In this study, a series of PHs that differed in their volume fraction of the internal phase in the emulsion templates was prepared (see Table 1, entries 1–4 for the detailed composition of the emulsion templates).



Scheme 2. Schematic illustration for the synthesis of macroporous matrixes by high internal phase emulsion polymerization.

Synthesis and functionalization of mesoporous silica nanoparticles

Mesoporous silica nanoparticles (MSNs) with random pore structure were synthesized by using the ammonia-catalyzed hydrolysis of TEOS in aqueous solution.^[37] Briefly, CTAB (0.91 g) and ammonium fluoride (NH₄F, 1.5 g) were dissolved in DI water (250 mL). This solution was heated to 80 $^\circ\text{C},$ and of TEOS (4.5 mL) was slowly added to it. The mixture was stirred continuously at 80 °C until the hydrolysis was completed. The prepared white powder was further dispersed into the solution of ethanol (200 mL) and hydrochloric acid (HCl, 37.5%; 4.0 mL) and heated at reflux at 90°C for 24 h. This procedure was repeated two times to make sure that the surfactants were completely removed. The obtained products were centrifuged and washed with DI water. To functionalize MSNs with acid and base groups, the organosilane, that is, MPTMS and APTMS, were grafted onto the surface of MSNs. The typical procedure was carried out as follows: as-prepared MSN (1.0 g) samples were dehydrated at 70 °C for 4.0 h under a nitrogen flow, and heated at reflux with APTES (1.2 mL) at 120 °C in toluene (20 mL) for 16 h. The obtained products (MSNs-SH) were filtered, washed with a mixture of diethyl ether and dichloromethane (1:1, v/v), and dried at 50°C for 24 h in air. Then, MSNs-SH was oxidized to become MSNs-SO₃H by using a modified published procedure.^[38] Typically, MSNs-SH (0.5 g) was added to the mixture of 30% hydrogen peroxide (10 mL), DI water (10 mL), and methanol (10 mL). The mixture was stirred at room temperature for 12 h. After that, the resultant precipitate was collected by filtration, washed with DI water several times, and dried under vacuum. The resulting sample was named MSNs-SO₃H. For the preparation of bifunctional MSNs exhibiting both acid and base groups (denoted as MSNs-SO3H-NH₂), APTMS was grafted onto the presynthesized MSNs-SO₃H by using the same grafting process as previously mentioned. In the comparison experiments, silica nanoparticles (SNs) and acid-base bifunctionalized SNs-SO₃H-NH₂ were also prepared in this study (the synthesis procedure is shown in the Supporting Information).

Integration of bifunctional silica particles and PH matrixes

The integration of bifunctional silica particles and PH matrixes was completed through the chemical reaction between amine and epoxy groups. Briefly, MSNs-SO₃H-NH₂ or SNs-SO₃H-NH₂ (0.2 g) was added to DMF (100 mL), and then macroporous PHs monoliths (1.0 g) were added. The mixture was stirred at 45 °C for 24 h under a nitrogen flow. After cooling to room temperature, the mixture was filtered and washed with ethanol and DI water twice. After drying at 50°C for 48 h, hierarchically macro-/mesoporous PHs@MSNs-SO₃H-NH₂ or PHs@SNs-SO₃H-NH₂ was obtained. In the subsequent sulfonation process, PHs@MSNs-SO₃H-NH₂ or $PHs@SNs\text{-}SO_3H\text{-}NH_2$ (0.5 g) was dispersed in $98\,\%$ sulfuric acid (50 mL). After stirring for 12.0 h at 70 $^\circ$ C, the sample was washed with a large amount of water until the filtrate was neutral and then dried at 50 $^\circ\text{C}$ for 24 h. The obtained catalysts were denoted as SPHs@MSNs-SO₃H-NH₂ and SPHs@SNs-SO₃H-NH₂, respectively. For comparison, sulfonated poly(HIPE) (SPH) was also synthesized by using the same sulfonation process, with all other parameters kept the same.

Catalyst characterization

A confocal laser scanning microscope (CLSM, Leica, TCSSP5II, Germany) was used for fluorescence testing. Morphology investigations were analyzed by means of field emission SEM, which was



carried out with an electron microscope equipped with a field emission electron gun and EDS. The morphology of the MSNs was characterized by TEM. BET specific surface areas, total pore volumes, and the average pore widths of the catalysts were determined from the adsorption and desorption isotherms of N₂ using a Micromeritics TriStar II 3020 instrument. Prior to characterization, the samples were degassed under a N₂ stream for 12.0 h. The specific surface area of the samples was calculated by applying the BET theory to the nitrogen-adsorption data within the P/P_0 range. Pore-size distributions were calculated from the desorption branch of the corresponding nitrogen isotherms, by applying the BJH method. TGA of samples was performed with a Netzsch Simultaneous Thermal Analyzer STA 449C (crucibles: aluminum from Netzsch) under a nitrogen atmosphere and a heating rate of 10°C min⁻¹ from 30 to 800°C. The organic functional groups of the catalyst were characterized with solid-state nuclear magnetic resonance spectroscopy (Bruker DSX-400WBNMR spectrometer, NMR/ Solid 400). The XPS measurements were carried out on a Thermo ESCALAB 250 with an accuracy of 0.3 eV. $\text{AI}_{\text{K}\alpha}$ radiation was used as the radiation source (1486.6 eV), and the recorded spectra were calibrated by the characteristic binding energy (BE) peak at 284.9 eV belonging to the C 1s region. For the Fourier transform infrared (FTIR) experiment, a mixture of the sample and the vacuum-dried IR-grade KBr with a weight ratio of 1:100 was pressed into a disk, and then recorded with a transmission mode using a Nicolet NEXUS-470 FTIR apparatus (USA) equipped with a DTGS detector using 64 scans and a resolution of $4\,cm^{-1}$ in the range from 400 to 4000 cm⁻¹. The elemental composition was recorded by using a vario EL III elemental analyzer (Elementar, Hanau, Germany). The concentration of sulfur in the final products was measured by ICP-AES analysis. For pyridine-IR studies, the sample was saturated with pyridine vapor in a closed vessel at 25 °C for 2.0 h, and desorption spectra were recorded at elevated temperatures. TPD of NH₃ or CO₂ was carried out on a TP 5000-II multiple adsorption apparatus (Tianjin Xianquan Corporation of Scientific Instruments, China). During the NH₃-TPD operation, the sample (100 mg) was pretreated in a helium atmosphere at 40 $^\circ\text{C}$ for 1.0 h. When the mass baseline was stable, the helium flow was stopped, and NH₃ was introduced until adsorption of the samples was saturated. Then, purging with helium was performed to remove residual NH₃ from the surface of the sample. Subsequently, the sample was heated from 40 to 400 $^\circ\text{C}$ under flowing helium at a rate of 10° Cmin⁻¹ for NH₃ desorption. The acidity of the catalyst was measured by the amounts of desorbed NH₃, which were calculated based on Equation (1)

$$Q = N_Q \times \frac{A}{A_{\rm T}} \times 100\% \tag{1}$$

in which $Q_{\rm N}$ [µmol g⁻¹] is the total amount of desorbed NH₃, and *A* is the corresponding deconvolution area of one NH₃-desorption peak, $A_{\rm T}$ is the total deconvolution area of all the NH₃-desorption peaks, and Q [µmol g⁻¹] is the amount of desorbed NH₃ corresponding to the TPD peak of relative area *A*. The basic feature was determined by means of CO₂-TPD using the same operation process as that described for NH₃-TPD above except NH₃ was replaced with CO₂.

Typical procedure for the catalytic conversion of cellulose into HMF

In this study, the ionic liquid (IL) [EMIM]Cl was employed in the cellulose hydrolysis process to break the β -1,4-glycosidic bonds of the

polymer, which is an essential step for the conversion of cellulose and opens up the possibility for subsequent catalytic transformations.^[39] Experiments were carried out in a 25 mL graduated Pyrex glass tube immersed in an oil bath preheated at the required temperature using a hot plate with a digital magnetic stirrer. The cellulose conversion included two steps of pretreatment and catalytic reaction. In a typical experiment for pretreatment, cellulose (0.1 g) was added to [EMIM]Cl (2.0 g), and the whole mixture was heated at 120 °C and stirred at 800 rmin⁻¹ for 0.5 h, so as to dissolve the cellulose. For a typical reaction step, the catalyst (40 mg) was added into the cellulose/[EMIM]Cl solution while maintaining heating and stirring at 800 rmin⁻¹ under the optimized conditions. The conversion process for glucose and fructose was the same as that for cellulose except exclusion of the pretreatment step, and the solvent was replaced by DMSO/H₂O (1:1 v/v).

Analysis methods

HMF was analyzed by a 1200 Agilent high-performance liquid chromatography (HPLC) instrument equipped with an Agilent TC-C18(2) column (4.6 \times 250 mm, 5.0 μm) and UV detector at 283 nm. During this process, the temperature of the column remained constant at 25 °C, and the mobile phase was methanol/water (7:3, v/v) at a flow rate of 0.7 mLmin⁻¹, and 22.5 μ L of each sample was injected manually. The concentration of HMF was calculated based on the standard curve obtained with pure HMF (Figure S2 in the Supporting Information). Fructose and glucose were analyzed by using the 1200 Agilent HPLC instrument fitted with a refractive index detector and Biorad column HPX 87H (7.8 mm×300 mm). During this process, the column temperature remained constant at $65 \degree$ C, while the applied mobile phase was $0.001 \ M H_2$ SO₄ at a flow rate of 0.55 mL min⁻¹. The product yield, selectivity, and conversion of the substrate were calculated based on Equations (2), (3), and (4) as follows:

HMF yield [mol%] =
$$\frac{\text{moles of HMF obtained}}{\text{moles of initial cellulose}} \times 100$$
 (2)

Substrate conversion
$$[\%] = \frac{\text{moles of reacted substrate}}{\text{moles of initial substrate}} \times 100$$

= $\frac{(\text{moles of initial substrate}) - (\text{moles of final substrate})}{\text{moles of initial substrate}} \times 100$
(3)

$$\label{eq:HMF} \text{HMF selectivity} \ [\%] = \frac{\text{moles of HMF obtained}}{\text{moles of reacted substrate}} \times 100 \qquad (4)$$

Recyclability of catalysts

The recycling efficiency of the catalyst was determined according to the dehydration of cellulose to HMF. After the reaction, the flask was cooled to room temperature, and the catalysts were separated from the reaction mixture by filtration and centrifugation, washed 10 times with a mixture of deionized water and ethanol, and dried at 80 °C for 24 h in a vacuum oven. Subsequently, the obtained recycling catalysts were reused for four consecutive cycles to produce HMF from cellulose under reaction conditions that were the



same as that of the fresh experiments. The HMF yield was determined from each run.

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