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Nafion-Resin-Modified Mesocellular Silica Foam Catalyst for 5-Hydroxymethylfurfural Production from D-Fructose

Zhen Huang, Wenya Pan, Haibo Zhou, Feng Qin, Hualong Xu, and Wei Shen*^[a]

Catalytic dehydration of D-fructose to 5-hydroxymethylfurfural (HMF) was investigated over a series of Nafion-modified mesocellular silica foam (MCF) materials. By using an impregnation method, Nafion resin was highly dispersed in the ultra-large pores of the MCFs. Highly efficient and selective dehydration of D-fructose to HMF was achieved in dimethyl sulfoxide solvent; an 89.3% HMF yield with 95.0% selectivity was obtained in the presence of the Nafion(15)/MCF catalyst. The effects of

Introduction

Replacing the diminishing petroleum-based resources and controlling global warming caused by the overuse of fossil fuels are becoming critical challenges for the current world. To achieve this, renewable biomass can serve as promising alternatives for the sustainable supply of valuable chemical intermediates and fuels.^[1] For example, 5-hydroxymethylfurfural (HMF) can be selectively oxidized into 2, 5-furandicarboxylic acid, which is suggested as an alternative raw material to the terephthalic or isophthalic acids that are used in the manufacture of polymers.^[2] In this context, catalytic processes for the conversion of biomass has become an attractive research issue over the last decade.^[3-5] Considering that the manufacturing of fine chemicals is derived from petroleum processing, the catalytic transformation of sugars or nonedible lignocellulosic materials into value-added compounds and liquid fuels has great significance for society in the future.^[6-10] As reported in the literature, many acidic catalysts have been used for the synthesis of HMF from fructose and glucose. Dumesic et al.^[1] and Raines et al.^[8] used homogeneous acids such as HCl and H₂SO₄ to catalyze the dehydration of p-fructose with a moderate HMF yield of 40-80% in different solvents [e.g., dimethyl sulfoxide (DMSO), methyl isobutyl ketone (MIBK), and N,N-dimethylacetamide (DMAc)]. In recent years, more attention has focused on ionic liquids for their excellent catalytic performance.[11-15] In addition, some special conditions for the dehydration of sac-

[a] Z. Huang, W. Pan, H. Zhou, F. Qin, Prof. H. Xu, Prof. W. Shen Department of Chemistry Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials and Laboratory of Advanced Materials Fudan University Shanghai, 200433 (PR China) Fax: (+86)21-65641740 E-mail: wshen@fudan.edu.cn Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201200967.

reaction temperature, reaction time, and solvent on the dehydration of D-fructose were systematically investigated. The catalyst could be regenerated through an ion-exchange method and a high yield was retained after being used five times. As a heterogeneous catalytic process, a possible reaction mechanism for the dehydration of D-fructose over Nafionmodified MCF catalysts was proposed.

charides, such as subcritical, supercritical, and microwave-assisted systems, were adopted to improve the yield of HMF.^[6, 16-19] However, these processes involve expensive ionic liquids and solvents, high-cost and complicated separation processes, and, in some cases, high energy consumption owing to the high temperatures that are required, which become barriers to commercial applications. In contrast, heterogeneous catalytic processes have advantages such as straight-forward catalyst separation and catalyst regeneration, as well as a comparatively low cost, which make them more applicative in industrial production. Therefore, many heterogeneous catalysts such as acidic ion-exchange resins,[16,20-22] Hform zeolites,^[23,24] sulfated zirconia,^[25,26] and supported heteropolyacids^[27] have been studied for the catalytic dehydration of hexoses. However, relatively high reaction temperatures or ionic liquids as co-solvents are necessary to help improve the catalytic performance of these solid catalysts. Herein, there are more essential needs for a catalyst that can express effective catalytic performance under mild conditions and in simple reaction systems.

Nafion perfluorosulfonic acid resin is a strong solid acid polymer with an acid strength comparable to that of pure sulfuric acid.^[28] However, the application of unswollen Nafion resin is limited because it has a low surface area, which is about 0.02 m²g⁻¹, whereas the acid density of Nafion is about 1.0 mmolg⁻¹.^[28,29] Commercialized Nafion NR50, with a pellet diameter of 0.6-1.5 µm, was used as a catalyst for the preparation of HMF from fructose, and a moderate HMF yield (45%-68%) was obtained.^[22,30] Accordingly, many materials with large surface areas have been used as carriers for Nafion. Over the past twenty years, Nafion resin has been widely applied in many organic reactions. Harmer et al. developed a Nafion resin/silica nanocomposite by using a porous silica network in which Nafion particles were entrapped.^[31] The activity of Nafion resin was enhanced in this material, which could be at-



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tributed to the increased density of available acid sites. Similar advantages were observed when SBA-15, SBA-16, MCM-41, and other mesoporous silica materials were used to synthesize catalysts containing Nafion resin through impregnation or a onepot synthesis.^[32-36] In our previous studies, Nafion-modified mesoporous materials exhibited good activity as a catalyst for the alkylation of isobutane with 1-butene. The materials with three-dimensional structures outperformed the ones containing a one-dimensional channel, which could be attributed to the improved diffusion ability of molecules in a three-dimensional mesostructure system.[33, 34] Among the numerous types of



Figure 1. Nitrogen adsorption-desorption isotherms (left) and SAXS patterns (right) of the MCF and Nafion-modified MCF materials with different Nafion loadings.

silica-based porous materials, mesocellular silica foams (MCFs), with well-defined ultra-large mesopores connected by uniformly sized windows, have unique advantages as catalyst supports.^[37] For example, large molecules are able to diffuse through the pores (up to 50 nm in diameter) of MCFs, and the mass transfer of reactants and products can easily be achieved because of its open continuous three-dimensional system.^[38, 39] The structural stability and reusability of MCFs have led to their wide application as catalyst carriers in recent years; however, they are rarely used in acidic catalysis processes.^[40-45]

Herein, based upon the acidic properties of Nafion resin and the ultra-large mesoporous MCFs, a series of Nafion-resin-supported MCF solid acid catalysts with different Nafion loadings are reported, which were prepared by using an impregnation method. Nitrogen adsorption and TEM–energy dispersive X-ray (EDX) studies indicated very good dispersion of Nafion nanospheres in the ultra-large mesopores. These catalysts showed excellent catalytic performance for the dehydration of p-fructose to HMF. The effects of Nafion loading, reaction temperature, and solvent on the catalytic activity were investigated. Moreover, the catalysts could be recycled and regenerated through an ion-exchange method, and a high yield was retained after being used for five times.

Results and Discussion

Preparation and characterization of the catalysts

In the present work, materials were prepared with three different Nafion loadings [Nafion(X)/MCF, in which X=15, 30, or 45 wt%] by using the impregnation method, which is described in detail in the Experimental Section. The nitrogen adsorption–desorption isotherms and small angle X-ray scattering (SAXS) patterns of MCF and Nafion/MCF materials are depicted in Figure 1. The textural parameters of the Nafion-modified

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materials, deduced from the nitrogen isotherms, are summarized in Table 1. MCF showed a steep H1-type hysteresis loop at high relative pressure, indicating a mesoporous material with large pore size and narrow pore-size distribution, which was substantiated by the SAXS pattern of MCF.^[46] The narrow

Table 1. Textural properties for Nafion modified MCF mesostructured ma- terials.						
Catalyst	S _{BET} ^[b]	D _{pore} ^[a]	$V_{pore}^{[a,b]}$	D _{win} ^[a]	S' _{BET} ^[b]	$V'_{\rm pore}^{[a,b]}$
	[m ² g ⁻¹]	[nm]	[cm ³ g ⁻¹]	[nm]	[m ² g ⁻¹]	[cm ³ g ⁻¹]
MCF	323	41.8	2.24	15.8	323	2.24
Nafion(15)/MCF	298	28.1	1.63	15.6	322	1.92
Nafion(30)/MCF	228	29.8	1.31	15.7	326	1.87
Nafion(45)/MCF	173	28.0	0.86	15.5	315	1.56
[a] Total pore diameter (D_{pore}) and V_{pore} were calculated by using the Barrett–Joyner–Halenda (BJH) adsorption branch of the nitrogen isotherm,						

and the window diameters (D_{win}) were calculated by using the BJH desorption branch. [b] S'_{BET} and V'_{pore} were calculated per gram of MCF, whereas S_{BET} and V_{pore} were calculated per gram of materials (i.e., MCF + Nafion).

type IV hysteresis loops and the SAXS patterns of all samples were maintained after the impregnation of Nafion resin with different loadings, indicating that the structure of the MCF was retained after modification. As an increasing amount of the Nafion resin was introduced into the network of the MCF, the Brunauer–Emmett–Teller surface area (S_{BET}) and the pore volume (V_{pore}) gradually decreased. However, when S_{BET} and V_{pore} were recalculated per gram of MCF, it was observed that V_{pore} decreased from 2.24 to 1.56 cm³g⁻¹, whereas S_{BET} was almost unchanged, as the Nafion loading increased from 15 to 45 wt%. From the pore-size-distribution analysis, the most probable pore diameter decreased from 42 to about 29 nm, whereas the size window remained at about 16 nm. It was pre-

viously reported that Nafion resin can disperse within the silicate lattice in the form of nanospheres with a diameter of 15-20 nm.^[36] In our studies, the results of the nitrogen sorption and SAXS analysis indicated that Nafion resin was dispersed inside the cells of the MCF as nanoparticles, and windows of MCF remained open even at a relatively high Nafion loading (e.g., 45 wt%), which resulted in unchanged S_{BET} and decreased V_{pore} per gram of MCF. When a cell holds a Nafion nanoparticle, it is unlikely to accommodate another one. Thus, the peak of pore-size distributions (Figure S1) in the MCF was centered at about 29 nm after modification with Nafion resin. With increased Nafion loading, the ratio of pores with 29 nm in diameter increased simultaneously. Compared with Nafion resin/ silica nanocomposite, the MCF had the ability to hold more Nafion molecules and its unique cells with windows in three directions could provide unobstructed space for molecular diffusion.

TEM images of Nafion-modified MCF materials in Figure 2 show the open mesostructured network interconnected with cells of uniform pore size. The structure of the MCF was preserved after impregnation of Nafion resin. In addition, the size of the mesocellular was well matched with that calculated from nitrogen sorption isotherms. Elemental mapping TEM– EDX images (Figure 2e–h) of Nafion(30)/MCF clearly showed that fluorine and sulfur were perfectly dispersed with silicon in the structure of the synthesized mesoporous materials, which was also in accordance with the results deduced from nitrogen adsorption–desorption studies.

The acidity-related properties of the Nafion-modified MCF materials and several commercial solid acid reference materials are detailed in Table 2. The Nafion loading was evaluated by using the elemental analysis method, which demonstrated an incorporation yield that referred to the percentage of Nafion resin deposited on MCF. The high incorporation yield, which ranged from 92% to 94%, was superior to that of Nafion/SBA-16 materials.^[34] The open mesocellular framework of the MCF enabled a more efficient diffusion of Nafion nanoparticles. The large-sized cells with a relatively narrow diameter window allowed independent and stable positioning of these nanoparticles. However, the H⁺ concentration, determined by using

Table 2. Acidic-related properties of Nafion-modified catalysts.					
Sample	Acia [mmol $H^+g_{cat}^{-1}$] ^[a]	dity [mmol S g _{cat} ⁻¹] ^[b]	Nafion incorporation [wt %] ^[c]		
Nafion(15)/MCF	0.142	0.141	94		
Nafion(30)/MCF	0.283	0.282	94		
Nafion(45)/MCF	0.432	0.415	92		
SAC-13	0.146	0.135	-		
Amberlyst-15	3.897	-	-		
SO_4^{2-}/ZrO_2	0.339	-	-		
Nafion(15)/	0.129	-	-		
MCF ^[d]			_		
[a] Titrated potentiometrically with 0.1 M NaOH after filtration and thor-					

ough washing (see the Experimental Section). [b] Calculated from elemental analysis. [c] Determined by comparing the amount of sulfur deposited and introduced. [d] Recycled and regenerated Nafion(15)/MCF catalyst after five uses.



Figure 2. TEM images of a) MCF, b) Nafion(15)/MCF, c) Nafion(30)/MCF, and d) Nafion(45)/MCF. EDX images of Nafion(30)/MCF: e) EDX map, and f) sulfur, g) silicon, and h) fluorine mapping.

a potentiometric titration, was similar to the concentration of sulfur, revealing that the active sites provided by the Nafion resin were highly accessible.

Catalytic performance of Nafion-modified MCF catalysts

Nafion-modified MCF materials and several reference solid acid catalysts were used for the catalytic dehydration of D-fructose into HMF. Their catalytic performances are summarized in Table 3. Among these results, an 89.3% HMF yield with 95.0% selectivity (entry 1) was obtained for Nafion(15)/MCF in DMSO at 90 °C after a reaction time of 2 h, which was much better

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Table 3. Catalytic performance of	different	catalysts	for	the	dehydration
of D-fructose to HMF in DMSO. ^[a]					

Entry	Catalyst	HMF yield [%]	Selectivity [%]	$STY^{[b]}$ [mol mol ⁻¹ h ⁻¹]
1	Nafion(15)/MCF	89.3	95.0	16.4
2	Amberlyst-15	26.3	76.2	3.7
3	SO ₄ ²⁻ /ZrO ₂	32.3	64.9	5.5
4	SAC-13	73.7	81.3	11.4
5 ^[c]	Nafion(15)/MCF	78.6	93.1	28.2
6 ^[c]	Nafion(30)/MCF	72.4	94.7	26.6
7 ^[c]	Nafion(45)/MCF	70.1	89.8	25.2
8	none	<2	-	-

[a] Reaction conditions unless otherwise stated: catalyst (acid amount: 0.06 mmol H⁺), p-fructose in DMSO (3 wt %, 12.5 g), 90 °C reaction temperature, and 2 h reaction time. [b] STY: HMF molar yield per molar unit of H⁺ of the catalyst per unit time. [c] Reaction conditions were the same except that the acid amount was 0.03 mmol H⁺.

than that of Amberlyst-15, SO_4^{2-}/ZrO_2 , and SAC-13 (entries 2–4) under the same conditions. Amberlyst-15 is a sulfonic acidic ion-exchange resin with nanoscale pores (≈ 25 nm in diameter) and comparatively weak acid strength. SO_4^{2-}/ZrO_2 is a strong solid acid with an amorphous pore structure, and SAC-13 is a Nafion resin/silica nanocomposite with 13–16 wt% Nafion entrapped within the amorphous silica porous network. This result indicated that the higher acid strength and the three-dimensional, open, ultra-large mesoporous system could improve the dehydration of D-fructose to HMF in DMSO. The structure of the MCF materials could promote efficient mass transfer of the reactants to the active sites and the products out of the pore system, which resulted in Nafion/MCF materials of high efficiency in the process.

The catalytic performances of Nafion/MCF catalysts with different Nafion loadings were also investigated. A lower acid content (0.03 mmol) was used so that there was a significant difference. As a result, Nafion/MCF with 15 wt% Nafion loading was superior to the other catalysts, which could be attributed to the improved Nafion distribution on Nafion(15)/MCF. Although the MCF has a large volume to hold the Nafion resin, some Nafion could adsorb onto the external surface of the framework. As the loading increased, the relative content of Nafion on the outside of the framework also increased, leading to inferior activities. Consequently, the HMF yield dropped from 78.6% to 70.1% when the Nafion loading was increased from 15 to 45 wt% (entries 5-7), whereas the space-time yield (STY) demonstrated that the efficiency of catalyst was also decreased from 28.2 to 25.2 mol mol⁻¹ h⁻¹. For comparison, a blank experiment was performed without any catalyst and the yield of HMF was less than 2% (entry 8). Finally, Nafion/ MCF was tested with a high initial concentration of D-fructose to simulate a practical application (Table S2). It could be seen that the HMF yield reached 78.9% and 69.5% in 10 and 20 wt% fructose solutions, respectively. The advantages of the Nafion/MCF material highlighted its potential applied value for the biomass transformation.

The effect of the reaction time on the conversion and HMF yield for the dehydration of D-fructose catalyzed by Nafion(30)/

MCF is shown in Figure 3 A. The HMF yield increased rapidly to 60% in 30 min, whereas the conversion of D-fructose reached over 70%. After a reaction time of 2 h, the HMF yield and D-fructose conversion gradually reached 87% and 96%, respec-



Figure 3. a) Effect of the reaction time, and b) effect of reaction temperature on the dehydration of D-fructose. The reaction conditions were similar to that of Table 3, entry 1 with Nafion(30)/MCF as the catalyst.

tively, and finally reached 90% and 97% after 3 h. This yield was higher than that of many other solid acid catalysts under similar conditions, even at a higher temperature. The catalytic performance of Nafion/MCF for the dehydration of D-fructose to HMF was outstanding compared to that of the ionic-liquid CrCl₂/EMIMCI system.^[47,48] The effect of reaction temperature with Nafion(30)/MCF is presented in Figure 3B. It can be seen that the HMF yield and selectivity gradually increased with temperature when the temperature was below 90°C. A high HMF yield of 88% with a selectivity of 91% was achieved at 90°C, and it was nearly unchanged up to 120°C. This reflected that the Nafion/MCF strong solid acid was an efficient catalyst, which could dehydrate D-fructose under mild conditions.

Effect of solvent on the activity of D-fructose dehydration

A series of solvents with different boiling points, including isopropanol, diacetone alcohol, MIBK, DMAc, and DMSO, were used to study the effect of the solvent on the activity of D-fructose dehydration. From the results (Table 4), it was demonstrated that the best fructose conversion (96.4%) and HMF yield (87.6%) were achieved in DMSO by using Nafion(30)/MCF and a reaction time of 2 h at 90 °C, whereas MIBK presented a moderate HMF yield of 16.4% under the same conditions. Very poor yields were obtained in isopropanol, diacetone alcohol, and DMAc. As reported in the literature, DMSO is suitable for the production of HMF from sugars.^[49] It acted as both an electron acceptor and an electron donator to improve the dehydration of fructose. In isopropanol and diacetone alcohol, a stable intermediate β -p-fructopyranoside was formed under the acidic conditions, which could not be further dehydrated into HMF.^[50] DMAc, as a stable and water-miscible aprotic sol-

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Table 4. Dehydration of D-fructose in different solvents. ^[a]					
Entry	Solvent	D-fructose conversion [%]	HMF yield [%]		
1	isopropanol	88.6	5.3		
2	diacetone alcohol	74.4	8.8		
3	MIBK	56.8	16.4		
4	DMAc	18.7	4.4		
5	DMSO	96.4	87.6		
6	MIBK/DMSO ^[b]	94.7	48.5		
[a] Reaction conditions: Nafion(30)/MCF (0.2 g), D-fructose (0.375 g), solvent (12.125 g), at 90 $^{\circ}$ C for 2 h. [b] Volume ratio of MIBK/DMSO=5:1.					

vent, could bind the free H⁺ in the solvent (control experiments conducted, see Table S1). It could adsorb on the acid sites of the catalyst, especially on the strongly acidic Nafion resin, to inhibit or block the reaction, which resulted in a 4.4% HMF yield. In contrast, MIBK resulted in a better yield; however, the dehydration of fructose could be limited by the solubility of D-fructose in MIBK under relatively mild conditions. Considering that MIBK was primarily used as an extraction solvent and DMSO was difficult to separate from the products, a two-component solvent system including MIBK and DMSO was used for the dehydration reaction, which aimed to optimize the isolation process of HMF by reducing the amount of DMSO used. The influence of MIBK/DMSO ratios on fructose conversion and HMF yield was investigated, and when 86% of DMSO was replaced with MIBK, a moderate HMF yield (48.5%) was achieved (see Table S4).

Investigation on the catalyst recycling

Nafion resin could be recycled easily and regenerated by using an ion-exchange method. The Nafion/MCF catalyst was used five times to study the stability of the catalyst; control experiments with SAC-13 as the catalyst were performed under the same conditions. The method of catalyst regeneration is described in detail in the Supporting Information. The results are presented in Figure 4, and it could be seen that the yield of HMF decreased slightly (about 6%) over catalyst Nafion(15)/ MCF after being reused five times, whereas the fructose conversion and HMF yield on SAC-13 were noticeably deceased. This indicated that Nafion/MCF was a stable solid acid, which benefited from the high dispersion of nanoparticles in the cells and the open continuous three-dimensional structure. The unobstructed molecule transfer route in the open mesocellular framework of the MCF enabled Nafion/MCF to be easily regenerated. Generally, the decrease in catalytic activity could be attributed to minor leaching of the Nafion resin (less than 10%, see Table 2) or acid site occupation by the byproducts that were produced after each run.

Possible mechanism for dehydration of ${\rm D}\mbox{-} fructose$ over Nafion/MCF catalysts

Based on the above results, the HMF yield in the dehydration of D-fructose was determined by many factors under the con-



Figure 4. Recycling of the Nafion(15)/MCF catalyst in the dehydration of Dfructose. The reaction conditions were same as that of Table 3, entry 1.

ditions we adopted. As a heterogeneous catalysis process, the reaction was not only affected by the acidic properties and structure of the catalyst, but also by the interaction between the reactant and the solid catalyst. The diffuse reflectance infrared Fourier transform (DRIFT) analysis (Figure S7) showed that the interactions between fructose and the MCF, such as electrostatic effects and hydrogen bonds from the polar silanol-rich surface of the MCF, could weaken the stability of the hydroxyl group and C-H bonds in fructose. This influence facilitated the dehydration of D-fructose and would have been greatly enhanced when Nafion, which is of strong electron-attractive ability, was used in the cells of the MCF. Thus, the dehydration of D-fructose was largely promoted on Nafion/MCF and the catalytic performance of Nafion-modified MCF materials was much better than the other strong solid acidic materials that were investigated. A possible mechanism for the dehydration of D-fructose catalyzed by Nafion-modified MCF composite materials was proposed according to a literature reference (Scheme 1).^[51] The protonation of the hydroxyl group caused by protonic acidity and the influences on chemical bonds were both taken into account. Once the fructofuranoses were formed and moved into the cells of the MCF, the protonation of the hydroxyl group on the saturated carbon could occur quickly. Because of the strong interaction with Nafion and silanol groups, loss of the first water molecule could become more efficient, leading to the formation of enediol intermediates. After deprotonation, under the influence of electrostatic forces and/or hydrogen bonding on the C-O and C-H bonds, the intermediate could continue to lose two water molecules to form HMF with high efficiency and selectivity. Moreover, the structural space limitation of MCF was helpful to inhibit the side reactions, which formed soluble polymers and insoluble humins in this system.

Conclusions

Nafion-resin-modified mesocellular silica foams are firstly prepared through an impregnation method. Within the open



Scheme 1. Possible mechanism for the dehydration of D-fructose over Nafion-modified MCF materials.

three-dimensional MCF framework, Nafion nanoparticles are highly dispersed in the ultra-large mesopores. In addition, an 89.3% HMF yield with a high selectivity of 95.0% is obtained from the dehydration of D-fructose when Nafion(15)/MCF is used as a strong solid acid catalyst in DMSO at 90 °C for 2 h. The outstanding catalytic performance is not only ascribed to the strong acid strength of Nafion but also to the open ultralarge pore system of the MCF. DSMO provides a more suitable environment and presents a better performance in the dehydration of D-fructose to HMF. Moreover, the Nafion/MFC catalyst can be easily recycled and regenerated. Based on the results, a possible mechanism for D-fructose dehydration to HMF over Nafion-modified MCF solid acid is proposed.

Experimental Section

Reagents and materials: Triblock copolymer pluronic P123 (EO₂₀PO₇₀EO₂₀, *M*_W = 5800), HMF (used as the standard sample), Amberlyst-15, SAC-13, and all solvents used in this work were purchased from Sigma–Aldrich. Naifon resin solution (5 wt% Nafion in water-alcohol solution) was purchased from Dupont. Tetraethyl orthosilicate (TEOS), 1,3,5-trimethylbenzene (TMB), p-Fructose, zirconium hydroxide, anhydrous ethanol, concentrated sulfuric acid, and aqueous HCI were purchased from Shanghai Chemical Co. All chemicals were used directly without further treatment. Pure water was obtained through an ultra-pure water system (Millipore, 18.2 M Ω cm at 298 K). The catalyst SO₄^{2–}/ZrO₂ was synthesized as previously reported.^[26]

Catalyst preparation: The pure siliceous as-synthesized MCF sample was prepared following the synthesis procedure described by

Zhao et al.^[52] In a typical synthesis, pluronic P123 (8.0 g, 1.38 mmol) was dissolved in HCl (1.6 m, 300 mL) solution, followed by addition of TMB (8.0 g, 67 mmol) and NH₄F (0.092 g, 2.48 mmol). After increasing the reaction temperature to 313 K, TEOS (17.6 g, 84 mmol) was added. The solution was stirred at 40 °C for 20 h before it was transferred into an autoclave for aging treatment at 130 °C for 24 h. Next, the white precipitates were collected through filtration and dried at room temperature for a further 24 h. The template P123 was removed from the as-synthesized MCF by using a Soxhlet extractor and ethanol over 48 h.

The Nafion-modified catalysts were prepared by impregnating Nafion in the above prepared MCF. The solid was dried at 80 °C for 12 h before it was mixed with ethanol and Nafion resin solution. The mixture was heated at 50 °C to gradually remove the solvents; the water and alcohols were subsequently evaporated under vacuum at 60 °C for 12 h. The resultant materials were denoted as Nafion(X)/MCF, in which X indicates the theoretical weight percent of Nafion loading (in this work, three Naifon loadings were studied, that is, X = 15, 30 or 45).

Catalyst characterization: Nitrogen sorption isotherms were performed by using a Quantachrome Quadrasorb SI analyzer. SAXS measurements were performed on a NanoSTAR SAXS system with CuK_a radiation ($\lambda = 0.154$ nm, 40 kV, 35 mA). TEM images and TEM-EDX element mapping were obtained on a JEOL 2100F microscope operated at 200 kV. The DRIFTs spectra were recorded on a Thermo Nicolet 6700 Fourier-transform infrared spectrometer equipped with a highly sensitive mercury cadmium telluride (MCT) detector, cooled by using liquid nitrogen. The ion-exchange capacities of Nafion-modified materials (corresponding to acid site concentration) were determined through potentiometric titrations with aqueous solutions of NaCl and NaOH.^[53]

Catalytic performance: In a typical reaction protocol for the dehydration of D-fructose, a 3 wt% fructose/DMSO solution containing D-fructose (0.37 g) was charged into a 50 mL flask, followed by the addition of the catalyst (0.2 g). The reaction was performed at 90 °C for 2 h with magnetic stirring. The point of zero time was taken to be when the reaction temperature reached the set point. After the reaction, the mixture was cooled and placed in a centrifuge for 15 min at a rate of 8000 rpm. The upper, clean solution was extracted and diluted 20 times with water before HPLC analysis. Before each reaction, a control sample for HPLC analysis was taken from the 3 wt% fructose/DMSO solution and diluted 20 times with water.

Product analysis and HPLC measurement: The composition analysis of the reaction mixture was conducted on a Shimadzu HPLC system equipped with refractive index detector. The saccharide and HMF were quantified by using HPLC with a Shodex SH1011 sugar column (300×8.0 mm, 6μ m), sulfuric acid ($0.0005 \,$ m in water) as the mobile phase at a flow rate of $0.8 \,$ mLmin⁻¹, and a column temperature of $50 \,^{\circ}$ C. Herein, the yield of HMF and the conversion of D-fructose were obtained by using an external standard method and then following Equation 1:

 $HMF \text{ selectivity} = \frac{HMF \text{ yield}}{D-\text{fructose conversion}}$ (1)

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