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Formyl-Modified Polyaniline for the Catalytic Dehydration of Fructose to 5-Hydroxymethylfurfural

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We report an unprecedented solid organic-base catalyst, formyl-modified polyaniline (FS-PAN), for the dehydration of fructose to 5-hydroxymethylfurfural (HMF) with a high yield of 90.4 mol%. We demonstrate that the nitrogen atoms incorporated between the phenyl rings in the backbone of the polyaniline chain contribute to the basicity of the catalyst. The grafting of electron-withdrawing formyl groups to the imine nitrogen atoms leads to a significant increase of basicity of the polymer catalyst owing to the greater localization of electrons at the amide nitrogen atom formed. A linear dependence of the yield of HMF on the grafting level of formyl groups in FS-PAN indicates that the amide acts as the active phase. A possible reaction mechanism for this organic-base-catalyzed dehydration reaction is proposed. The side-reaction of HMF rehydration is inhibited thoroughly, and the condensation of any reaction intermediates to undesirable oligomers is restrained by this base catalyst. This organic-base catalyst can be recycled completely without loss of activity. This research highlights the first application of a highly effective and stable solid base catalyst for the transformation of renewable carbohydrates into fine chemicals.

Introduction

Renewable biomass-derived sugars are good alternatives to diminishing fossil resources for the synthesis of bulk chemicals and transportation fuels.[1] The development of effective methods to convert naturally available C_6 sugars to useful and polyfunctional molecules, such as 5-hydroxymethylfurfural (HMF), is of great significance for biorefinery.[2]

As a versatile and key platform chemical, HMF is produced mainly through the acid-catalyzed dehydration of C_6 sugars.[3] Recent efforts have been devoted to the development of solid acid catalysts to meet the recyclability issue.[4] However, the Brønsted acid sites in solid acids are prone to deactivation or leaching by water formed in the dehydration step, and these problems can be limited by using Lewis acid catalysts instead of Brønsted acids.[5] However, HMF can be further rehydrated to levulinic acid (LA) and formic acid (FA) by the acid catalysis;[6] thus, the process requires the continuous extraction of HMF from the reaction solution by an organic solvent,[7] the continuous extraction of water under reduced pressure,[8] or the stabilization of HMF by an appropriate solvent to increase the selectivity to HMF.[9] Successful catalysts that allow high selectivity and satisfactory stability for the dehydration of hexose are still limited.

The use of solid base catalysts for hexose dehydration may result in cleaner reactions because of the lack of acid sites. However, strongly alkaline conditions should be avoided as they promote the degradation of the monosaccharide to more than 50 different byproducts.[10] Although organic-base catalysts (i.e., amines) have been achieved the glucose-to-fructose isomerization with high yields and selectivities,[11] few examples have focused on the dehydration of fructose to HMF. The development of effective solid base catalysts for fructose dehydration will open up a new avenue to the highly selective synthesis of HMF from biomass-derived saccharides.

Polyaniline is the first conducting polymer in which a nitrogen atom is incorporated between the phenyl rings in the backbone of the polymer chain. The electronic properties of polyaniline can be adjusted through acid/base doping or oxidation/reduction treatments,[12] which result in significant differences to its properties. Polyaniline is a hybrid of benzenoid amine ($-NHC_6H_4-$) and quinoid diimine ($-N{=}C_6H_4{=}N-$) structures (Scheme S1),[13] whereas H_2SO_4-doped polyaniline (S-PAN, Scheme 1 a) is conductive owing to the delocalization of π-electrons through the “protonated quinone imine” structure.[14] The imine nitrogen atoms are protonated preferentially because the imine nitrogen atom is more basic than the amine nitrogen atom.[15]

Herein, we report that the grafting of formyl groups onto the quinoid imine nitrogen atoms of S-PAN to endow the polymer catalyst (i.e., formyl-modified polyaniline, abbreviated as FS-PAN, Scheme 1 b) with a significantly higher basicity, which results in a high HMF yield of 90.4 mol% for the catalytic dehy-

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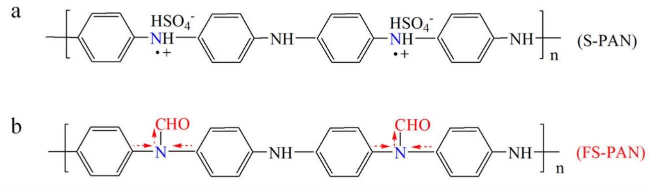


Scheme 1. The structures of (a) S-PAN and (b) FS-PAN. The red arrows indicate the direction of electron flow in the polymer catalyst. The presence of benzenoid amine units in FS-PAN is omitted but presented in Scheme S2.[13]

dration of fructose in DMSO. The structure, activity, and recyclability of this solid base catalyst are evaluated. We show that the solid organic-base catalyst is highly selective and stable during the dehydration process. A possible reaction mechanism for this organic-base-catalyzed dehydration reaction is proposed. The side-reaction of HMF rehydration to LA is suppressed thoroughly, the condensation of any reaction intermediates to undesirable oligomers is limited, and fructose is converted completely in this base-catalyzed system.

Results and Discussion

Catalyst preparation and characterization

We synthesized the catalyst precursor S-PAN through the oxidative polymerization of aniline with ammonium persulfate (APS) in dilute aqueous H_2SO_4 solution at 5 °C.[16] The oligomers and any possible byproducts formed in the polymerization process were removed by repeated washing with water, methanol, and diethyl ether. To prepare the FS-PAN catalyst, S-PAN was reacted with formaldehyde solution (40 wt %, $n_{HCHO}/n_{AN}=24$) at 140 °C for 4 h, and the product was washed with water and dried at 100 °C overnight.

The morphologies of the S-PAN precursor and FS-PAN catalyst were characterized by SEM (Figure 1 a and b). Both of them are irregular aggregates of polyaniline nanoparticles (≈450 nm) with diameters of 100 to 300 μm. The BET surface areas of S-PAN and FS-PAN were determined to be 21.6 and 25.5 $m^2 g^{-1}$, respectively, and their average pore diameters were 1.4 and 1.3 nm (Table S1).[13] The XRD pattern of S-PAN shows the typical amorphous structure of doped polyaniline with two diffraction peaks centered at $2\theta \approx 21$ and 25.5°, whereas a broad diffraction peak centered at $2\theta \approx 24°$ for FS-PAN corresponds to a dedoped (deprotonated) polyaniline structure (Figure 1 c).[17] These results indicate the occurrence of deprotonation during the modification of S-PAN with formaldehyde. The elemental analysis revealed that the doping level of H_2SO_4 in S-PAN is approximately 18.0 %, whereas nearly no sulfur atoms exist in the backbone of the FS-PAN catalyst (Table S2);[13] this confirms the complete removal of H_2SO_4 from S-PAN after the formaldehyde treatment.

We used FTIR spectroscopy to characterize the structures of the catalysts (Figure 1 d). For S-PAN, the band at $\tilde{\nu}=1570$ cm^{-1} corresponds to the C=C ring stretching vibration of the quinone units, whereas the band at $\tilde{\nu}=1483$ cm^{-1} with a shoulder at $\tilde{\nu}=1380$ cm^{-1} is assigned to the C=C ring stretching vibration of the benzenoid structure.[18] It is generally accepted that the relative peak intensity I_{1570}/I_{1483} is indicative of the extent of oxidation in polyaniline.[12a] The band at $\tilde{\nu}\approx 1293$ cm^{-1} originates from the C−N stretching of secondary aromatic amines, whereas the band at $\tilde{\nu}\approx 1236$ cm^{-1} is related to protonated C−N groups. The band at $\tilde{\nu}\approx 1116$ cm^{-1} corresponds to the C−H aromatic in-plane bending and is often related to the doped structure; therefore, the relative peak intensity I_{1116}/I_{1293} reflects the doping level of polyaniline. Moreover, the band at $\tilde{\nu}\approx 792$ cm^{-1} originates from the C−H out-of-plane bending in 1,4-disubstituted ring structures and indicates the occurrence of the *para* coupling of aniline during the polymerization. In comparison with the S-PAN spectrum, we found clear shifts from $\tilde{\nu}\approx 1293$ to 1330, 1483 to 1504, and 1570 to 1606 cm^{-1}, respectively, in the FTIR spectrum of FS-PAN. These upshifts can be explained by the occurrence of deprotonation,[19] as indicated by the XRD and element analysis results. Furthermore, the significant decrease of I_{1116}/I_{1330} compared with I_{1116}/I_{1293} for S-PAN confirms the dedoping of FS-PAN from S-PAN by formaldehyde. Furthermore, a decrease in I_{1606}/I_{1504} compared with I_{1570}/I_{1483} suggests the reduction of quinoid to benzenoid structures. That is, in addition to deprotonation, the modification of S-PAN with formaldehyde also leads to the further reduction of polyaniline. Notably, we observed two new infrared bands centered at $\tilde{\nu}=1676$ and 1256 cm^{-1}; the former band corresponds to the amide C=O stretching and suggests that formyl groups have been introduced to the FS-PAN catalyst. The band at $\tilde{\nu}=1256$ cm^{-1} could not be assigned to the stretching of protonated C−N groups of the deprotonated catalyst; therefore, it is rationally related to a new form of C−N stretching, probably amide C−N stretching. That is, the new formyl groups in FS-PAN are most probably grafted onto the quinoid imine nitrogen atom during the formaldehyde treatment.

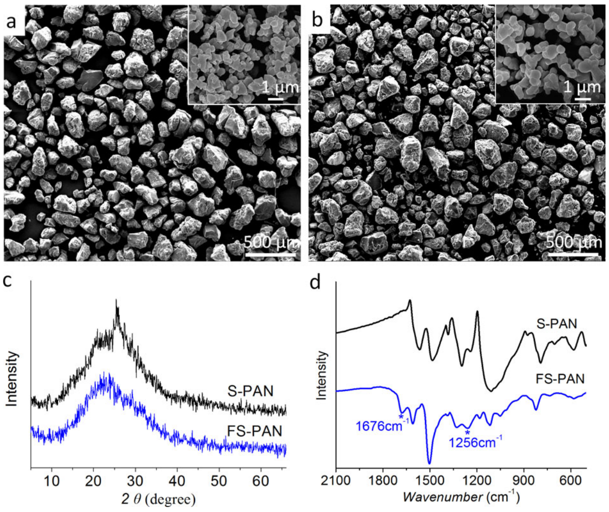


Figure 1. SEM images of (a) S-PAN and (b) FS-PAN (inset: SEM images, for which the catalysts were sonicated); (c) XRD patterns of S-PAN and FS-PAN; (d) FTIR spectra of S-PAN and FS-PAN.

The S-PAN and FS-PAN were further characterized by X-ray photoelectron spectroscopy (XPS). The benzenoid amine, quinoid imine, protonated imine, polarized quinoid imine, and formyl-grafted amine structures in polyaniline can be differentiated quantitatively in the deconvoluted N 1s XPS spectrum. For S-PAN (Figure 2 a), the N 1s XPS spectrum is deconvoluted to three components at binding energies (BEs) of 399.3, 400.9, and 402.8 eV, which are assigned to benzenoid groups (−NH−), radical cations ($-N^{\bullet+}=$), and cations ($-N^{+}H=$), respectively.[20] The surface contents of these three kinds of nitrogen species were evaluated to be 70.7 (399.3 eV), 25.6 (400.9 eV), and 3.7 % (402.8 eV), and these results indicate the existence of polarons/bipolarons owing to the protonation of quinoid imines. As a consequence, the peak at BE = 398.2 eV for imine nitrogen atoms is not observed. For FS-PAN (Figure 2 b), only two components at BEs of 399.3 and 400.2 eV are resolvable. The two peaks at BE > 400.9 eV are not resolvable, which supports the complete deprotonation of FS-PAN and is also consistent with the structure proposed on the basis of the FTIR results. The new peak at a BE of 400.2 eV is assigned to the amide nitrogen atoms originating from the grafting of the formyl groups to the imine nitrogen atoms. Theoretical simulations at the M06-2x/def2-tzvpp level support the above assignment (Figure S1).[13] Furthermore, the surface contents of the benzenoid amine nitrogen and amide nitrogen atoms of approximately 86.7 and 13.3 %, respectively, indicate that the grafting level of formyl groups is approximately 13.3 %. The C 1s spectra of S-PAN and FS-PAN were also deconvoluted. For S-PAN (Figure 2 c), the main peak at a BE of 284.6 eV is assigned to the C−C/C−H groups present in the polymer in addition to the standard substance. The peaks at BEs of 285.9 and 288.5 eV are attributed to C−N and $C{=}N^{+}H$ groups, respectively. The shake-up satellite peak at BE = 291.2 eV is attributed to C−N groups in polymer.[21] For FS-PAN (Figure 2 d), three components at BE = 284.6, 285.9, and 287.7 eV are resolvable, and the latter one is assigned to the C=O groups that have been introduced through formaldehyde modification. Therefore, both the N 1s and the C 1s XPS results confirm the grafting of formyl groups to the imine nitrogen atoms of FS-PAN.

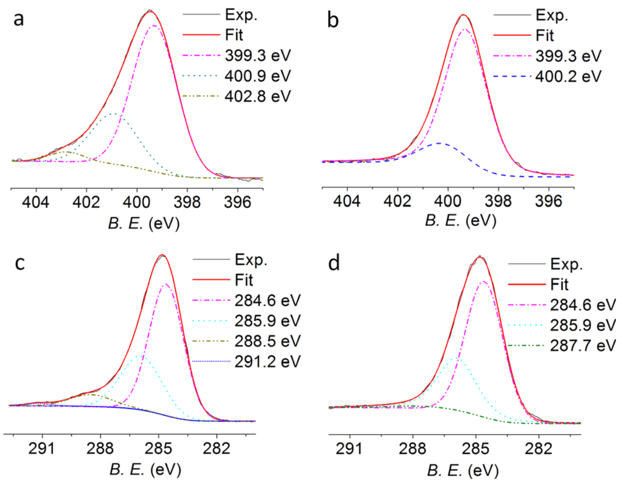


Figure 2. Deconvoluted N 1s XPS spectra of (a) S-PAN and (b) FS-PAN; deconvoluted C 1s XPS spectra of (c) S-PAN and (d) FS-PAN.

We subsequently used ESR spectroscopy to study the electron spins in S-PAN and FS-PAN (Figure S2, curves a and g).[13] The obtained spectra can be described with simple peak-to-peak linewidths (ΔH_{pp}) and average *g* values, as listed in Table 1. For the untreated S-PAN (Entry 1), we observe two lines with average *g* values of approximately 2.0025, which are assigned to typical π radicals in conjugated carbon systems. This result is consistent with the unpaired spin delocalized primarily on the N-incorporated phenyl rings.[22] For FS-PAN (Entry 7), the *g* value increases to 2.0035, a typical value for heteroatom systems,[23] which indicates that the spins become more localized at the nitrogen sites.[24] In addition, we also observed the broadening of ΔH_{pp} from 3.9 G for S-PAN to 16.1 G for FS-PAN, which qualitatively supports the greater localization of charge carriers at the amide nitrogen atoms of FS-PAN.[25] As a result, the basicity of the FS-PAN catalyst is enhanced owing to the higher electron density at the amide nitrogen atom.

Table 1. Results from ESR and FTIR spectroscopy of FS-PAN catalysts obtained through the treatment of S-PAN with formaldehyde for different times.[a]

Entry	Treatment time [h]	*g*	ΔH_{pp} [G]	I_{1116}/I_{1330}	I_{1606}/I_{1504}	I_{1676}/I_{1330}
1	0	2.0025	3.9	1.29	0.85	0
2	0.25	2.0031	2.5	1.05	0.62	0.34
3	0.5	2.0032	3.1	1.00	0.60	0.62
4	1.0	2.0035	15.4	0.97	0.60	0.72
5	2.0	2.0035	15.4	0.96	0.57	0.72
6	3.0	2.0035	16.1	0.96	0.54	0.72
7	4.0	2.0035	16.1	0.96	0.48	0.73
8	–[b]	2.0029	13.8	0.71	0.87	0

[a] Treatment conditions: S-PAN (1 g), formaldehyde solution (20 mL, 40 wt %, $n_{HCHO}/n_{AN} = 24$), stirring, 140 °C. [b] D-PAN obtained by treating S-PAN with aqueous ammonia.

We also studied the FTIR spectra of the FS-PAN catalysts prepared by treating S-PAN with formaldehyde for different times to get detailed information on their structural variations. The results are presented in Figure S3,[13] and the characteristic peak intensities are listed in Table 1. The values of I_{1116}/I_{1330}, I_{1606}/I_{1504}, and I_{1676}/I_{1330} represent the doping level, oxidation level, and grafting level of the FS-PAN catalysts, respectively. Within 1 h, I_{1116}/I_{1330} and I_{1606}/I_{1504} decrease rapidly with time, and this reflects a fast deprotonation from S-PAN and the reduction of the quinone moieties to form phenyl rings. After 1 h, I_{1116}/I_{1330} does not vary, but I_{1606}/I_{1504} still displays a slight decreasing tendency, which indicates the ongoing reduction of the quinone structure owing to the excess of formaldehyde in the system. Accordingly, I_{1676}/I_{1330} exhibits an increasing tendency from 0 to 1 h; the value reaches a maximum value at 1 h and then remains almost invariable over 1 to 4 h. This intensity variation reflects the fast grafting of the formyl groups within the first 1 h. That is, the reaction of formaldehyde with S-PAN starts with the removal of the dopant (sulfuric acid), followed by the grafting of formyl groups to the imine nitrogen atoms and the gradual quinoid to benzenoid reduction.

The ESR spectra of these FS-PAN catalysts obtained with different modification times were also studied to reveal the electronic characters of the catalysts during the formaldehyde treatment (Figure S2).[13] The *g* values and ΔH_{pp} values obtained from the ESR spectra are also listed in Table 1; the *g* values of these FS-PAN catalysts increase significantly within 1 h (Entries 1 to 4) and then remain unchanged from 1 to 4 h (Entries 5 to 7). The increase of the *g* value within 1 h reveals the fast localization of electrons at the nitrogen sites, which may not be caused by the reduction of polyaniline because the occurrence of reduction after 1 h does not lead to a further increase of the *g* value. As we could not determine whether the localization of electrons at the nitrogen sites is induced by the deprotonation of the dopant or grafting of the formyl group, we prepared a deprotonated polyaniline (D-PAN) to solve this problem by treating S-PAN with excess aqueous ammonia. The FTIR and ESR spectra of D-PAN are shown in Figures S4 and S5,[13] respectively. The lower I_{1116}/I_{1330} ratio compared with that of S-PAN is indicative of the successful deprotonation of D-PAN. The *g* value and ΔH_{pp} for D-PAN are 2.0029 and 13.8 G, respectively (Table 1, Entry 8). The smaller *g* value of D-PAN than that of FS-PAN demonstrates that the localization of charge carriers at the nitrogen atoms of the FS-PAN catalyst is not induced mainly by the deprotonation of S-PAN but may be caused by the grafting of formyl groups to the imine nitrogen atoms. We observed the gradual broadening of ΔH_{pp} from 3.9 to 16.1 G during the formaldehyde treatment from 0 to 4 h; the initial narrowing of ΔH_{pp} within 0.5 h may be derived from the promotion of the mobility of electrons in the polymer chain backbone because of the coexistence of dopant and electron-withdrawing formyl groups.

Table 2. Catalytic dehydration of C_6 sugars to HMF over polyaniline-based catalysts.[a]

Entry	Catalyst	Conversion [mol %]	Y_{HMF} [mol %]	Y_{DFF} [mol %]	Y_{LA} [mol %]	Y_{FA} [mol %]
1	S-PAN	100	44.9	7.2	9.2	12.1
2	FS-PAN	100	90.4[b]	0.4	–	3.5
3[c]	FS-PAN	89.7	6.4	–	–	4.7
4[d]	FS-PAN	100	42.9	0.5	–	27.2
5[e]	FS-PAN	100	52.3	0.5	–	9.5
6	D-PAN[f]	100	36.4	–	–	1.4
7	P-PAN[g]	100	21.9	–	–	1.3
8[h]	FS-PAN	100	84.5	1.9	–	6.6
9[i]	FS-PAN	100	84.6	1.4	–	9.4
10[j]	FS-PAN	100	64.2	1.0	–	9.1

[a] Reaction conditions: fructose (45 mg), catalyst (30 mg), DMSO (1 mL), 140 °C, 4 h. [b] TON = 5.3 based on the amide nitrogen atoms. [c] Glucose as the substrate. [d] Sucrose as the substrate. [e] Inulin as the substrate. [f] D-PAN was prepared by treating S-PAN with aqueous ammonia for deprotonation. [g] P-PAN was prepared by treating D-PAN with phenylhydrazine to reduce the quinoid imine to benzenoid amine. [h] Acetone as the additive ($n_{acetone}/n_{fructose} = 3:1$). [i] DHA as the additive ($n_{DHA}/n_{fructose} = 3:1$). [j] Glycerol as the additive ($n_{glycerol}/n_{fructose} = 3:1$).

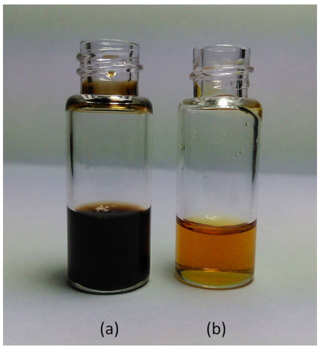


Figure 3. Images of the products from the catalytic dehydration of fructose over (a) S-PAN and (b) FS-PAN.

Activity comparison of S-PAN and FS-PAN

The catalytic performances of S-PAN and FS-PAN for fructose dehydration were studied in DMSO at 140 °C for 4 h (Table 2, Entries 1 and 2). Over the S-PAN catalyst precursor, an HMF yield of 44.9 mol % was obtained, and the formation of byproducts such as FA (12.1 mol %), LA (9.2 mol %), 2,5-formylfuran (DFF, 7.2 mol %), and furfural (0.3 mol %) was observed. The resulting mixture was dark (Figure 3 a). The simultaneous formation of FA and LA indicates the occurrence of HMF rehydration in the dehydration system. The formation of DFF, the oxidized product from HMF, reveals the oxidative nature of S-PAN, as is consistent with the FTIR spectroscopy results. The appearance of a small amount of furfural is indicative of the direct C—C cleavage of fructose in DMSO.[26] The carbon balance was evaluated to be 62.0 %. As fructose was completely converted, the carbon imbalance indicates the formation of insoluble humins or soluble oligomers. The low selectivity (44.9 %) of HMF in this S-PAN-catalyzed system may be attributed to the presence of sulfuric acid that has been doped in the polymer chain. That is, several side-reactions, such as the rehydration of HMF and the condensation of any reaction intermediates, occur owing to the presence of a Brønsted acid, even in the well-known polar aprotic solvent DMSO that is frequently used to stabilize HMF.[9a]

Significantly, if FS-PAN was used as the catalyst, a clear orange mixture (Figure 3 b) afforded a higher HMF yield of 90.4 mol %. The yield of DFF decreased to 0.4 mol %, which implies that the oxidative ability of the FS-PAN catalyst is reduced owing to the reduction of a quinoid imine to a benzenoid amine structure during formaldehyde modification. FA (3.5 mol %) was the main byproduct detected. However, no LA was produced; therefore, the rehydration of HMF is restrained thoroughly in this base-catalyzed system, and the formed FA may be produced directly from the decomposition of fructose.[27] The carbon balance increased from 62.0 % (for S-PAN) to 91.6 % for this organic-base catalyst. However, this FS-PAN catalyst exhibits low activity for the catalytic dehydration of glucose to HMF (Table 1, Entry 3), possibly because of the low catalytic activity for glucose-to-fructose isomerization in DMSO. For sucrose or inulin as the substrate, HMF yields of 42.9 and 52.3 mol %, respectively, were obtained on the basis of the conversion of the monosaccharide (Table 1, Entries 4 and 5);

therefore, the FS-PAN catalyst is active for the dehydration of fructose units under the reaction conditions applied.

Identification of the active phase for fructose dehydration

We are interested in the high activity and selectivity of the FS-PAN catalyst. To discern whether the catalytic activity originates from the deprotonation of the Brønsted acid, the reduction of the quinoid diimine, or the grafting of formyl groups on FS-PAN, we prepared a reductive form of polyaniline (i.e., P-PAN) by treating D-PAN with phenylhydrazine for activity comparison. The lower I_{1596}/I_{1494} ratio in the FTIR spectrum of P-PAN reveals the transformation of the quinoid imine structure to the benzenoid amine structure in P-PAN (Figure S6).[13] The yields of HMF over D-PAN and P-PAN were 36.4 and 21.9 mol%, respectively (Table 2, Entries 6 and 7). Hence, for the four polyaniline-based catalysts, the activity order towards fructose dehydration is FS-PAN > S-PAN > D-PAN > P-PAN. Considering the structures of these catalysts, we tentatively infer that the high activity of FS-PAN is not derived from the dedoping or reduction of the polyaniline backbone but may originate from the grafting of formyl groups to the imine nitrogen atom. Specifically, the activity of the formed amide nitrogen atom is higher than that of the imine nitrogen atom, and the latter is more active than the amine nitrogen atom.

To illustrate the above point, in control experiments, we synthesized a series of FS-PAN catalysts by varying the amount of formaldehyde used to modify the S-PAN precursor. The FTIR spectra of the as-synthesized FS-PAN catalysts are plotted in Figure S7.[13] The I_{1676}/I_{1330} ration, representative of the grafting level of formyl groups in FS-PAN, increases significantly as the molar ratio of formaldehyde to aniline monomer (n_{HCHO}/n_{AN}) increases, reaches a maximum at $n_{HCHO}/n_{AN} = 24$, and then remains unchanged with further increase of n_{HCHO}/n_{AN} to 36. Correspondingly, the yield of HMF exhibits the same variation tendency as the n_{HCHO}/n_{AN} ratio changes (Figure 4a); this reveals a close correlation between the catalytic activity and the grafting level of formyl groups in the FS-PAN catalysts. Similarly, the activity of another series of FS-PAN catalysts prepared by varying the time of formaldehyde modification is presented in Figure 4b. The yield of HMF increased significantly as the treatment time increased from 0 to 1 h and then remained invariable after 1 h. This activity variation is consistent with the change of the grafting level in the FS-PAN catalysts (as illustrated in Table 1). Notably, the positive linear dependence of the yield of HMF on the grafting level of formyl groups (expressed as I_{1676}/I_{1330} from the FTIR spectra) for all of the as-synthesized FS-PAN catalysts is summarized in Figure 4c, which indicates that a higher grafting level of formyl groups in FS-PAN allows a higher HMF yield. The results reveal strongly that the amide formed by the grafting of formyl groups is the active phase for the dehydration of fructose to HMF. The maximum turnover number (TON) was determined to be 5.3 relative to the amide nitrogen atoms. From these results in combination with the ESR analysis results, it is reasonable to assume that the high activity of FS-PAN is caused by the enhanced basicity of the polymer catalyst owing to the presence of electron-withdrawing formyl groups at the amide nitrogen atom. A more basic FS-PAN catalyst may favor the interaction between fructose and the catalyst to initiate the dehydration reaction.

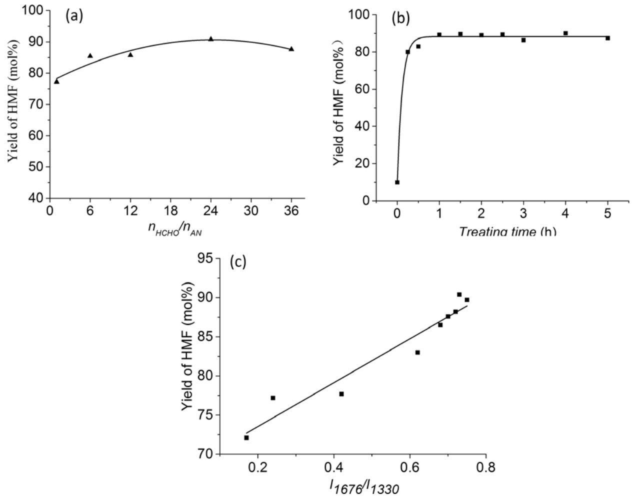
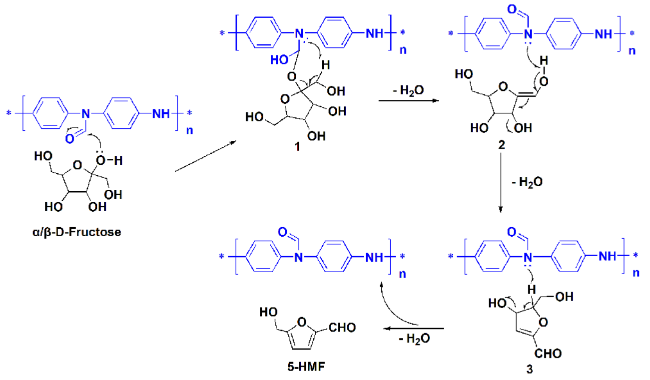


Figure 4. Yields of HMF over FS-PAN catalysts prepared by varying (a) the ratio of formaldehyde to aniline monomer (n_{HCHO}/n_{AN}) and (b) the treatment time with formaldehyde. (c) Linear dependence of HMF yield on the grafting level of formyl groups (expressed as I_{1676}/I_{1330}) in FS-PAN catalysts.

Possible reaction mechanism for the organic-base-catalyzed dehydration reaction

To date, much effort has been devoted to reveal the mechanism for the dehydration of fructose to HMF catalyzed by Lewis or Brønsted Acids. However, the catalytic system without H^+ (or metal) ions has not been studied fully. In a preliminary study on the mechanism of the FS-PAN-catalyzed dehydration reaction, we investigated the interactions between the FS-PAN catalyst and fructose by introducing additives (acetone, 1,3-dihydroxyacetone, or glycerol) with structures similar to those of acyclic or cyclic fructose (Figure S8).[13] The competitive interaction of FS-PAN with fructose and additive molecules will influence the dehydration of fructose to HMF. If acetone or 1,3-dihydroxyacetone was added, a slight decrease in HMF yield was observed (Table 2, Entries 8 and 9); therefore, the catalyst interacts weakly with the carbonyl groups in acetone and 1,3-dihydroxyacetone. This result also suggests that fructose exists mainly in the form of cyclic furanose in DMSO, typically α/β-furanose, rather than the acyclic form.[9c] In contrast, the introduction of glycerol decreases the yield of HMF to 64.2 mol% (Table 2, Entry 10), which is indicative of the strong interaction of the hydroxy groups in fructose with FS-PAN. Therefore, we can assume rationally that the dehydration of fructose may be initiated by the interaction of the hydroxy groups in α/β-furanose with the amide structure in the FS-PAN catalyst.

A possible reaction mechanism for this organic-base-catalyzed dehydration reaction is proposed in Scheme 2; the 2-hydroxy oxygen atom with lone electron pairs in fructose reacts with the electrophilic amide carbon atom in FS-PAN to form intermediate **1**, followed by the release of one H_2O molecule with the aid of the lone electron pair of the amide nitrogen



Scheme 2. Proposed mechanism for the FS-PAN-catalyzed dehydration of fructose to HMF.

atom. Then, the formed enol intermediate **2** is converted into an aldehyde through keto–enol tautomerism and releases another H_2O molecule with the aid of the amide nitrogen atom. Subsequently, the amide nitrogen atom acts as a base to capture a proton connected to C5 of fructose to form intermediate **3**. Finally, a third H_2O molecule is released to produce HMF. Further investigations on the capture of the intermediates are underway.

Effect of reaction solvent and temperature

We studied the influence of the reaction solvent on the formation of HMF (Table S3). The results show that the reaction in *N*-methylpyrrolidone (NMP) produced a high HMF yield of 67.1 mol%. However, the dehydration of fructose in 1,4-dioxane, THF, and methyl isobutyl ketone (MIBK) resulted in lower HMF yields of 15.9–20.5 mol%. Possibly, NMP favors the dissolution of fructose and may promote further the interaction between fructose and the organic-base catalyst.

The effect of reaction temperature on the dehydration reaction was studied in the range 120 to 160 °C. The results plotted in Figure S9 reveal that the HMF yield increases significantly from 120 to 140 °C to reach a maximum value of 90.4 mol% at 140 °C and then decreases to 84.9 mol% as the reaction temperature increases further to 160 °C. The yield of the byproduct FA does not change clearly with the variation in reaction temperature; therefore, the slight decrease in HMF yield at elevated temperature indicates the aggregation of HMF to undesirable oligomers. In all cases, the absence of LA highlights the inhibition of HMF rehydration by the organic-base catalyst in various solvents and at various temperatures.

Recycling of the organic-base catalyst

The thermostability of the FS-PAN catalyst was studied by recording the FTIR spectra of the catalysts after calcination at different temperatures (140, 220, and 300 °C; Figure S10).[13] No clear differences were observed in the FTIR spectra of the fresh catalyst and the catalysts calcined at 140 and 220 °C, whereas the clear decrease of the intensity of the infrared band at $\tilde{\nu} = 1676\ \mathrm{cm}^{-1}$ in the spectrum of the catalyst calcined at 300 °C compared with that of the fresh FS-PAN catalyst indicates the dissociation of formyl groups from the polymer catalyst. Furthermore, a thermogravimetric (TG) study revealed that the FS-PAN catalyst begins to decompose at elevated temperature (up to ~400 °C, Figure S11).[13] Consequently, this polymeric FS-PAN catalyst is completely recyclable in four successive runs, and the HMF yield was least 85.8 mol% (Figure 5). The FTIR spectra of fresh and used FS-PAN catalysts show no clear differences (Figure S12).[13] These results demonstrate the high activity and stability of the solid organic-base catalyst in the presence of water.

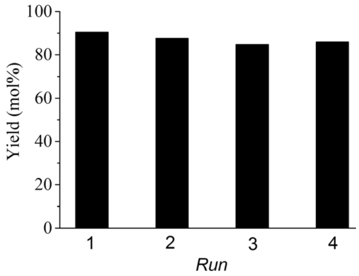


Figure 5. Recycling of FS-PAN catalyst for the catalytic dehydration of fructose to HMF. Reaction conditions: fructose (45 mg), catalyst (30 mg), DMSO (1 mL), 140 °C, 4 h.

Conclusions

We have demonstrated that the nitrogen heteroatoms incorporated between the phenyl rings in the backbone of the polyaniline chain contribute to the basicity of the catalyst. The delocalization of π electrons in H_2SO_4-doped polyaniline (S-PAN) results in lower electron density at the nitrogen atoms and lower basicity of the catalyst, which leads to a lower yield of 5-hydroxymethylfurfural (HMF, 44.9 mol%) from fructose dehydration in DMSO. However, the grafting of electron-withdrawing formyl groups to the quinone imine nitrogen atoms leads to greater localization of electrons at the amide nitrogen atom formed and significantly higher basicity of the formyl-modified polyaniline (FS-PAN) catalyst. As a result, the FS-PAN catalyst exhibits high catalytic activity and selectivity for HMF formation with complete conversion of fructose [$\mathrm{Yield}_{\mathrm{HMF}} =$ 90.4 mol%, turnover number (TON) = 5.3]. In addition, we have illustrated a positive linear dependence of the dehydration activity of FS-PAN on the grafting level of formyl groups. Notably, the rehydration of HMF to levulinic acid (LA) and the condensation of any reaction intermediates to undesirable oligomers are effectively inhibited in this base-catalyzed reaction system. The thermostability of FS-PAN allows its reuse for at least four runs without a clear decrease of activity. This research highlights the application of a highly selective and recyclable solid base catalyst for the transformation of renewable carbohydrates into fine chemicals.

Experimental Section

Materials

Formaldehyde (40 wt %), H_2SO_4 (98 %), aqueous ammonia (37 wt %) and analytical reagent (AR) grade aniline, APS, nitrobenzene, methanol, and diethyl ether were purchased from Kolong Chemical Company (Chengdu, China). 1,3-Dihydroxy acetone (98 %), AR-grade furfural, acetone, phenylhydrazine, and glycerol were purchased from J&K Chemical Co. Ltd. DMSO (AR grade) was obtained from Fuyu Fine Chemical Co., Ltd. (Tianjin, China). D-Fructose [bulk reagent (BR) grade] was purchased from REGAL Co. Ltd. FA (98 %) was purchased from Sigma–Aldrich. Glycerol (spectrophotometric grade) was purchased from Alfa Aesar. LA (98 %) was purchased from Acros Organics. DFF (98 %) was purchased from Tokyo Chemical Industry. Aniline was distilled before use. All of the other chemical reagents were used as purchased without further purification. Deionized (DI) water (resistance $> 18.2\ \mathrm{M\Omega\,cm^{-1}}$) was used in all experiments.

Catalyst preparation

The catalyst precursor S-PAN was synthesized through the oxidative polymerization of aniline in aqueous H_2SO_4 solution at 5 °C. In a typical synthesis, freshly distilled aniline (0.22 M) was dissolved in aqueous H_2SO_4 solution (0.78 M, 200 mL). Then, a solution of APS (0.78 M, 80 mL) was added slowly over 1 h to the above solution with the reaction temperature maintained below 5 °C, as the polymerization of aniline is strongly exothermic. After the complete addition, the mixture was stirred for another 30 min. The resultant precipitate (S-PAN) was separated by filtration, washed consecutively with water, methanol, and diethyl ether to remove the oligomers and any possible byproducts, and then dried at 100 °C overnight. To prepare the FS-PAN catalyst, S-PAN (1 g) was reacted with formaldehyde solution (20 mL, $n_{HCHO}/n_{AN} = 24$) at 140 °C for 4 h, and the product was washed with water three times and dried at 100 °C overnight. The deprotonated polyaniline catalyst (D-PAN) was prepared by treating S-PAN with excess aqueous ammonia at room temperature. The reductive polyaniline catalyst (P-PAN) was prepared by treating D-PAN with phenylhydrazine (Ph, $n_{Ph}/n_{AN} =$ 1:1) at 140 °C for 4 h.

To study the influence of formaldehyde treatment on the catalytic activity, two series of FS-PAN catalysts were prepared as follows: (1) FS-PAN*x* catalysts (*x* represents the treatment time) were prepared by varying the treatment time with HCHO with n_{HCHO}/n_{AN} kept at 24; (2) FS-PAN*y* catalysts (*y* represents the molar ratio of HCHO to AN) were prepared by varying the amount of HCHO used ($n_{HCHO}/n_{AN} = 1$–36).

Catalyst characterization

The SEM images were recorded with a low-vacuum SEM (FEI Inspect F) instrument. The catalyst samples were coated with gold before SEM observation. The N_2 physisorption isotherms of the catalysts were measured at −196 °C with a Micromeritics ASAP-2020 analyzer. The surface areas were determined with the BET equation. The pore volumes and average pore diameters were determined by the Barrett–Joyner–Halenda (BJH) method from the desorption branches of the isotherms. The XRD patterns were collected with a LTD DX-1000 CSC diffraction instrument operating at 40 kV and 25 mA with nickel-filtered $\mathrm{CuK_\alpha}$ radiation ($\lambda = 1.54056$ Å). The data were collected in the 2θ range 5–70° with a step of 0.0544° in continuous-scanning mode. Element analysis was performed with a Thermo Finnigan (FLASH, 1112 SERIES) instrument. The FTIR spectra of samples as KBr disks were recorded with a Nicolet Nexus 6700 spectrometer with a spectral resolution of $4\ \mathrm{cm^{-1}}$ in the wavenumber range $500–4000\ \mathrm{cm^{-1}}$ at room temperature. The XPS spectra were recorded with a XSAM800 spectrometer (KRATOS) with $\mathrm{AlK_\alpha}$ radiation (1486.6 eV) operating at 12 kV and 12 mA. The binding energy (BE) was calibrated with C 1s at 284.8 eV and was estimated to be accurate within 0.2 eV. A linear background was subtracted from all spectra. The ESR spectra were recorded at ambient temperature with a Bruker BioSpin ESR spectrometer. Thermogravimetric/differential thermogravimetric (TG/DTG) analysis was performed with a Netzsch TG209 instrument at a heating rate of $10\ \mathrm{K\,min^{-1}}$ with a nitrogen flow of $20\ \mathrm{mL\,min^{-1}}$.

Catalytic dehydration of fructose

All catalytic reactions were performed in pressure tubes heated in a temperature-controlled oil bath with magnetic stirring. In a typical reaction procedure, a 35 mL reaction tube was charged with fructose (45 mg), FS-PAN (30 mg), and DMSO (1 mL) in turn. The mixture was heated to 140 °C and incubated for 4 h. After the completion of the reaction, the mixture was cooled gradually to room temperature. The organic-base catalyst was separated from the resulting mixture by filtration.

In control experiments, additive compounds (acetone, DHA, or glycerol) were added together with fructose before the dehydration reaction. The molar ratio of the additive compound to fructose was 3:1, and the other reaction conditions were kept unchanged.

Product Analysis

HMF, DFF, and furfural from the liquid products were analyzed quantitatively by GC (FILI, GC-9700) with an Innowax capillary column (30 m × 0.25 mm), a flame ionization detector (FID), and a ZB-2020 integrator. Typical conditions for GC analysis were as follows: injector temperature 260 °C, detector temperature 270 °C, nitrobenzene as the internal standard. Byproducts such as FA and LA were analyzed quantitatively by HPLC (Dionex, UltiMate 3000 Series) with a Dionex PG-3000 pump, an Aminex HPX-87 column (Bio-Rad) (50 °C), a Shodex 101 refractive index detector (35 °C) and a variable-wavelength detector with H_2SO_4 (5 mM) as the mobile phase at a flow rate of $0.6\ \mathrm{mL\,min^{-1}}$. The yields of the products were calculated from external-standard curves constructed with authentic samples. The conversion of fructose, product yields, and the carbon balance were defined as follows: conversion of fructose (mol %) = (moles of fructose reacted)/(moles of starting fructose) × 100 %; yield of HMF (mol %) = (moles of HMF formed)/(moles of starting fructose) × 100 %; yield of byproduct (FA, LA, DFF, and furfural; mol %) = (moles of byproduct formed)/(moles of starting fructose) × 100 %; carbon balance (%) = (moles of carbon atoms in all products)/(moles of carbon atoms in starting fructose) × 100 %.

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[1] a) G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, *Science* **2005**, *308*, 1446–1450; b) J. R. Rostrup-Nielsen, *Science* **2005**, *308*, 1421–1422; c) J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem. Int. Ed.* **2007**, *46*, 7164–7183; *Angew. Chem.* **2007**, *119*, 7298–7318; d) R. M. West, Z. Y. Liu, M. Peter, J. A. Dumesic, *ChemSusChem* **2008**, *1*, 417–424; e) D. Esposito, M. Antonietti, *Chem. Soc. Rev.* **2015**, *44*, 5821–5835; f) J. Fan, M. De Bruyn, V. L. Budarin, M. J. Gronnow, P. S. Shuttleworth, S. Breeden, D. J. Macquarrie, J. H. Clark, *J. Am. Chem. Soc.* **2013**, *135*, 11728–11731; g) J. B. Binder, R. T. Raines, *J. Am. Chem. Soc.* **2009**, *131*, 1979–1985.

[2] a) O. O. James, S. Maity, L. A. Usman, K. O. Ajanaku, O. O. Ajani, T. O. Siyanbola, S. Sahu, R. Chaubey, *Energy Environ. Sci.* **2010**, *3*, 1833; b) A. A. Rosatella, S. P. Simeonov, R. F. M. Frade, C. A. M. Afonso, *Green Chem.* **2011**, *13*, 754–793; c) S. P. Teong, G. Yi, Y. Zhang, *Green Chem.* **2014**, *16*, 2015–2026.

[3] a) J. N. Chheda, Y. Román-Leshkov, J. A. Dumesic, *Green Chem.* **2007**, *9*, 342–350; b) X. Tong, Y. Li, *ChemSusChem* **2010**, *3*, 350–355; c) R. Karinen, K. Vilonen, M. Niemela, *ChemSusChem* **2011**, *4*, 1002–1016; d) K.-i. Shimizu, A. Satsuma, *Energy Environ. Sci.* **2011**, *4*, 3140–3153; e) T. Wang, M. W. Nolte, B. H. Shanks, *Green Chem.* **2014**, *16*, 548–572.

[4] a) I. V. Kozhevnikov, *J. Mol. Catal. A* **2007**, *262*, 86–92; b) M. J. Climent, A. Corma, S. Iborra, *Green Chem.* **2011**, *13*, 520–540; c) X. Qi, H. Guo, L. Li, R. L. Smith, Jr., *ChemSusChem* **2012**, *5*, 2215–2220; d) M. Hara, K. Nakajima, K. Kamata, *Sci. Technol. Adv. Mater.* **2015**, *16*, 034903–034924; e) H. Xu, Z. Miao, H. Zhao, J. Yang, J. Zhao, H. Song, N. Liang, L. Chou, *Fuel* **2015**, *145*, 234–240; f) Y. Peng, Z. Hu, Y. Gao, D. Yuan, Z. Kang, Y. Qian, N. Yan, D. Zhao, *ChemSusChem* **2015**, *8*, 3208–3212.

[5] a) K. Seri, Y. Inoue, H. Ishida, *Chem. Lett.* **2000**, *29*, 22–23; b) F. Wang, A.-W. Shi, X.-X. Qin, C.-L. Liu, W.-S. Dong, *Carbohydr. Res.* **2011**, *346*, 982–985.

[6] a) R. Weingarten, J. Cho, R. Xing, W. C. Conner, Jr., G. W. Huber, *ChemSusChem* **2012**, *5*, 1280–1290; b) Y. Liu, L. F. Zhu, J. Q. Tang, M. Y. Liu, R. D. Cheng, C. W. Hu, *ChemSusChem* **2014**, *7*, 3541–3547; c) V. Choudhary, S. H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N. S. Marinkovic, A. I. Frenkel, S. I. Sandler, D. G. Vlachos, *J. Am. Chem. Soc.* **2013**, *135*, 3997–4006.

[7] a) Y. Román-Leshkov, J. N. Chheda, J. A. Dumesic, *Science* **2006**, *312*, 1933–1937; b) Y. Yang, C. W. Hu, M. M. Abu-Omar, *Green Chem.* **2012**, *14*, 509–513; c) V. V. Ordomsky, J. van der Schaaf, J. C. Schouten, T. A. Nijhuis, *ChemSusChem* **2012**, *5*, 1812–1819.

[8] K.-i. Shimizu, R. Uozumi, A. Satsuma, *Catal. Commun.* **2009**, *10*, 1849–1853.

[9] a) G. Tsilomelekis, T. R. Josephson, V. Nikolakis, S. Caratzoulas, *ChemSusChem* **2014**, *7*, 117–126; b) V. Nikolakis, S. H. Mushrif, B. Herbert, K. S. Booksh, D. G. Vlachos, *J. Phys. Chem. B* **2012**, *116*, 11274–11283; c) A. S. Amarasekara, L. D. Williams, C. C. Ebede, *Carbohydr. Res.* **2008**, *343*, 3021–3024.

[10] a) B. Y. Yang, R. Montgomery, *Carbohydr. Res.* **1996**, *280*, 27–45; b) C. J. Knill, J. F. Kennedy, *Carbohydr. Polym.* **2003**, *51*, 281–300.

[11] a) C. Liu, J. M. Carraher, J. L. Swedberg, C. R. Herndon, C. N. Fleitman, J.-P. Tessonnier, *ACS Catal.* **2014**, *4*, 4295–4298; b) J. M. Carraher, C. N. Fleitman, J.-P. Tessonnier, *ACS Catal.* **2015**, *5*, 3162–3173; c) Q. Yang, S. Zhou, T. Runge, *J. Catal.* **2015**, *330*, 474–484; d) H. M. Mirzaei, B. Karimi, *Green Chem.* **2016**, *18*, 2282–2286.

[12] a) Y. Furukawa, F. Ueda, Y. Hyodo, I. Harada, T. Nakajima, T. Kawagoe, *Macromolecules* **1988**, *21*, 1297–1305; b) A. Varela-Álvarez, J. A. Sordo, G. E. Scuseria, *J. Am. Chem. Soc.* **2005**, *127*, 11318–11327.

[13] See Supporting Information for details.

[14] Y. Furukawa, T. Hara, Y. Hyodo, I. Harada, *Synth. Met.* **1986**, *16*, 189–198.

[15] a) J. C. Chiang, A. G. MacDiarmid, *Synth. Met.* **1986**, *13*, 193–205; b) E. T. Kang, K. G. Neoh, S. H. Khor, K. L. Tan, B. T. G. Tan, *J. Chem. Soc. Chem. Commun.* **1989**, 695–697; c) A. G. MacDiarmid, A. J. Epstein, *Synth. Met.* **1995**, *69*, 85–92.

[16] M. Nandi, R. Gangopadhyay, A. Bhaumik, *Microporous Mesoporous Mater.* **2008**, *109*, 239–247.

[17] J. P. Pouget, M. E. Jozefowicz, A. J. Epstein, X. Tang, A. G. MacDiarmid, *Macromolecules* **1991**, *24*, 779–789.

[18] Y. Cao, S. Z. Li, Z. J. Xue, D. Guo, *Synth. Met.* **1986**, *16*, 305–315.

[19] S. X. Xing, C. Zhao, S. Y. Jing, Z. Wang, *Polymer* **2006**, *47*, 2305–2313.

[20] a) G. M. do Nascimento, V. R. L. Constantino, R. Landers, M. L. A. Temperini, *Polymer* **2006**, *47*, 6131–6139; b) X.-L. Wei, M. Fahlman, A. J. Epstein, *Macromolecules* **1999**, *32*, 3114–3117.

[21] B. Sreedhar, P. Radhika, B. Neelima, N. Hebalkar, M. V. B. Rao, *Polym. Adv. Technol.* **2009**, *20*, 950–958.

[22] a) V. I. Krinichnyi, H. K. Roth, G. Hinrichsen, F. Lux, K. Luders, *Phys. Rev. B* **2002**, *65*, 155205; b) X. L. Wei, Y. Z. Wang, S. M. Long, C. Bobeczko, A. J. Epstein, *J. Am. Chem. Soc.* **1996**, *118*, 2545–2555.

[23] H. H. S. Javadi, R. Laversanne, A. J. Epstein, R. K. Kohli, E. M. Scherr, A. G. MacDiarmid, *Synth. Met.* **1989**, *29*, 439–444.

[24] S.-A. Chen, G.-W. Hwang, *Macromolecules* **1996**, *29*, 3950–3955.

[25] a) J. Joo, S. M. Long, J. P. Pouget, E. J. Oh, A. G. MacDiarmid, A. J. Epstein, *Phys. Rev. B* **1998**, *57*, 9567–9580; b) V. I. Krinichnyi, S. D. Chemerisov, Y. S. Lebedev, *Phys. Rev. B* **1997**, *55*, 16233–16244; c) G. M. do Nascimento, P. Y. G. Kobata, M. L. A. Temperini, *J. Phys. Chem. B* **2008**, *112*, 11551–11557; d) S. M. Yang, T. S. Lin, *Synth. Met.* **1989**, *29*, E227–E234.

[26] a) J. Zhang, E. Weitz, *ACS Catal.* **2012**, *2*, 1211–1218; b) J. Cui, J. Tan, T. Deng, X. Cui, Y. Zhu, Y. Li, *Green Chem.* **2016**, *18*, 1619–1624.

[27] a) T. D. Swift, C. Bagia, V. Choudhary, G. Peklaris, V. Nikolakis, D. G. Vlachos, *ACS Catal.* **2014**, *4*, 259–267; b) L. Yang, G. Tsilomelekis, S. Caratzoulas, D. G. Vlachos, *ChemSusChem* **2015**, *8*, 1291–1291.

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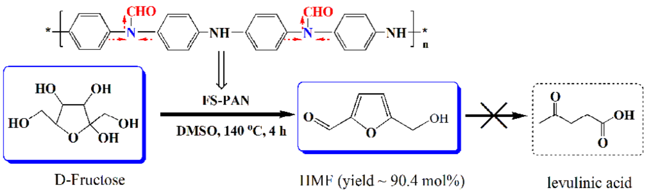

Out of the FS-PAN: An unprecedented solid organic-base catalyst, formyl-modified polyaniline (FS-PAN), is developed for the highly selective dehydration of fructose to 5-hydroxymethylfurfural (HMF). The side-reaction of HMF rehydration to levulinic acid is inhibited thoroughly, and the condensation of reaction intermediates to undesirable oligomers is restrained.

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Formyl-Modified Polyaniline for the Catalytic Dehydration of Fructose to 5-Hydroxymethylfurfural