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Acid-Catalyzed Dehydration of Fructose into 5-Hydroxymethylfurfural by Cellulose-Derived Amorphous Carbon

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Carbonaceous solid (CS) catalysts with $-SO_3H$, -COOH, and phenolic -OH groups were prepared by incomplete hydrothermal carbonization of cellulose followed by either sulfonation with H_2SO_4 to give carbonaceous sulfonated solid (CSS) material or by both chemical activation with KOH and sulfonation to give activated carbonaceous sulfonated solid (a-CSS) material. The obtained carbon products (CS, CSS, and a-CSS) were amorphous; the CSS material had a small surface area ($< 0.5 \text{ m}^2 \text{ g}^{-1}$) and a high $-SO_3H$ group concentration (0.953 mmol g⁻¹), whereas the a-CSS material had a large surface area ($514 \text{ m}^2 \text{ g}^{-1}$) and a low $-SO_3H$ group concentration (0.172 mmol g⁻¹). The prepared materials were evaluated as

catalysts for the dehydration of fructose to 5-hydroxymethylfurfural (5-HMF) in the ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM][CI]). Remarkably high 5-HMF yields (83%) could be obtained efficiently (80 °C and 10 min reaction time). CSS and a-CSS catalysts had similar catalytic activities and efficiencies for the conversion of fructose to 5-HMF in [BMIM][CI]; this could be explained by the trade-off between $-SO_3H$ group concentration (high for CSS) and surface area (high for a-CSS). The cellulose-derived catalysts and ionic liquid exhibited constant activity for five successive recycles, and thus, the methods developed provide a renewable strategy for biomass conversion.

Introduction

With increasing consumption and depletion of traditional fossil fuel reserves, efficient processes for biomass resources are essential for the sustainable development of chemicals and fuels.^[1] As an important biomass-derived platform chemical for plastics and fuels, the production of 5-hydroxymethylfurfural (5-HMF) by acid-catalyzed dehydration of fructose has been studied to evaluate the feasibility of initial proposals that report possible catalysts and reaction solvent systems.^[2–5]

To date, many acid catalysts have been proposed for the conversion of saccharides into 5-HMF, including mineral or organic acids, such as $H_2SO_{4^{\prime}}$ HCl, $H_3PO_{4^{\prime}}$ oxalic acid,^[5-7] H-form zeolites,^[8] transition-metal ions,^[4,9] and strong acid cation exchange resins.^[5,7,10,11] Homogenous acids are inexpensive and effective, but they have serious drawbacks related to product separation, solvent recycling, and equipment corrosion. Solid acid catalysts, such as H-form zeolites and metal phosphates, offer simplified separation and recycling, but still suffer from low conversion efficiencies (30–60%) for relatively long reaction times of 2 h.^[12] Strong acid cation exchange resins have been studied and are efficient for converting fructose into 5-HMF;^[10,13] however, these types of catalysts are limited to temperatures below 130 °C due to the thermal stability of the resin.^[14]

Biomass-derived sulfonated carbonaceous materials, which are typically prepared by pyrolytic treatment of sugar or cellulose feeds and subsequent sulfonation, are interesting candidates as solid acid catalysts because they have the potential to provide sufficient catalytic activity for many acid-catalyzed reactions,^[3, 15, 16] and could remove the temperature limitations of the polymeric resins used in ion-exchange catalysts. Compared with resin-type or oxide-type solid acid catalysts, sulfonated carbonaceous catalysts can be expected to be cheaper and more versatile than polymer substrates and they are apt to be robust under harsh reaction conditions.^[17] Toda et al. prepared a sulfonated sugar catalyst through the pyrolysis of glucose at 400 °C and showed that the catalyst had high activity for the synthesis of biodiesel from vegetable oil.^[15] They also synthesized a cellulose-derived, carbon-based solid acid at pyrolysis temperatures of 400–650 °C, and the catalyst obtained exhibited a high catalytic activity for esterification of ethanol with acetic acid.^[18]

Herein, cellulose-derived carbonaceous solids were prepared by hydrothermal carbonization of cellulose followed by sulfonation. The catalytic activity of the as-prepared carbonaceous solids was evaluated for the promotion of the formation of 5-HMF from fructose in an ionic-liquid solvent. Carbonaceous solid acid catalysts exhibited good activity for the reaction system (ca. 80% yield of 5-HMF from fructose) and maintained their activity for five cycles.

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Results and Discussion

Characterization of the catalyst

Figure 1 shows SEM images of carbon materials obtained by hydrothermal carbonization of cellulose with no post-treatment and with two post-treatment methods. From these



Figure 1. Typical SEM images of carbon materials obtained by hydrothermal treatment of cellulose: a) product without post-treatment, carbonaceous solid (CS); b) product with H₂SO₄ post-treatment, carbonaceous sulfonated solid (CSS); and c) product with KOH and H₂SO₄ post-treatment, activated carbonaceous sulfonated solid (a-CSS).

images (Figure 1), it can be seen that the obtained solid material from cellulose hydrothermal carbonization (CS) consisted mainly of aggregates of carbonaceous microspheres that had diameters of several µm. The smooth surfaces of the microspheres were partially destroyed after post-treatment sulfonation. When CS was chemically activated with KOH and sulfonated, a drastic morphological change occurred and the resulting a-CSS material had a spongelike structure with large conchoidal cavities.

XRD patterns for the samples (Figure 2) exhibited one strong diffraction peak at $2\theta = 10-30^{\circ}$ and one broad, but



Figure 2. XRD patterns of the CSS and a-CSS materials.

weak, peak at 35-50°. These XRD patterns are typical of amorphous carbonaceous materials that consist of aromatic carbon sheets oriented in a random fashion.[18]

FTIR spectra of CSS and a-CSS are shown in Figure 3. The band at 3400 cm⁻¹ is attributed to -OH stretching vibrations, which indicates that large numbers of hydroxyl groups are present on the as-prepared carbon materials.^[19] The absorption bands at 1716 and 1600 cm⁻¹ are attributed to COO⁻ and C=C stretching vibrations, respectively.^[20] The vibration bands at 1060 (SO_3^- stretching) and 1400 cm⁻¹ (O=S=O stretching in



Figure 3. FTIR spectra of CSS and a-CSS materials.

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 SO_3H) indicate that the as-prepared carbon materials have surface $-SO_3H$ groups^[16] and are likely to promote acid-catalyzed reactions. The prepared carbonaceous materials had an amorphous carbon structure that probably consisted of polycyclic aromatic carbon sheets with randomly attached SO_3H , COOH, and phenolic OH groups.

Composition analyses of the prepared carbonaceous materials are shown in Table 1. Inductively coupled plasma mass

Table 1. Characterization of CSS and a-CSS catalysts derived from hydro- thermal carbonization of cellulose.							
Catalyst	Composition	Yield [%] ^[a]	Surface area [m ² g ⁻¹]	SO_3H concentration [mmol g ⁻¹]			
CSS a-CSS	$\begin{array}{l} CH_{0.512}O_{0.635}S_{0.022} \\ CH_{0.825}O_{0.551}S_{0.004}K_{0.002} \end{array}$	27 10	<0.5 514	0.953 0.172			
[a] The yield is expressed as 1 g _{product} per 100 g _{cellulose} .							

spectrometry (ICP MS) and elemental analysis revealed that the obtained amorphous carbon materials had a chemical composition of $CH_{0.512}O_{0.635}S_{0.022}$ and $CH_{0.825}O_{0.551}S_{0.004}K_{0.002}$, respectively, for CSS and a-CSS. The corresponding amounts of SO₃H group for CSS and a-CSS (Table 1) were calculated to be 0.953 and 0.172 mmol g⁻¹, respectively, on the basis that all sulfur atoms in the sulfonated carbon material were present as SO₃H groups.^[16] It is estimated that the CSS samples had a Brunauer–Emmett–Teller (BET) surface area of about 0.5 m²g⁻¹ based on calculations from adsorption isotherms using the standard BET equation. However, the surface area of the carbon samples was greatly increased (514 m²g⁻¹) when they were subjected to chemical activation by KOH.

Conversion of fructose into 5-HMF with carbonaceous solids in an ionic liquid

The dehydration of fructose into 5-HMF catalyzed by various carbon materials prepared in this work was investigated (Figure 4). When CS was used as the catalyst in the reaction, no 5-HMF formation could be detected at 80 °C after 30 min. However, when CSS was used a 5-HMF yield of 77% could be obtained in 20 min; thus demonstrating good catalytic activity. Therefore, it is clear that the number of SO₃H acid groups in the catalyst plays a crucial role in the formation of 5-HMF from fructose.

The CS catalyst has a small surface area of less than $0.5 \text{ m}^2 \text{g}^{-1}$, which probably limits its catalytic activity. To improve the catalytic activity of the as-prepared carbon material, CS was chemically activated by thermal treatment with KOH with the hope of increasing its surface area. Additional sulfonation was used to introduce more SO₃H groups into the chemically activated material. Unfortunately, although the surface area of the obtained activated carbon material (a-CSS) increased to 514 m²g⁻¹, the amount of SO₃H groups could not be correspondingly increased, but dropped to 0.172 m²g⁻¹.



Figure 4. Yields of 5-HMF obtained from fructose in an ionic liquid catalyzed by carbonaceous materials derived by hydrothermal treatment of cellulose. Ionic liquid: 1-butyl-3-methylimidazolium chloride ([BMIM][CI]). Catalysts: CS (\triangle), CSS (\bullet), and a-CSS (\bigcirc). Reaction conditions: fructose (0.10 g), [BMIM][CI] (1 g), catalyst (0.05 g), 80 °C.

It has been shown that with increasing thermal treatment temperature for glucose carbonization, the obtained carbon materials are composed of larger carbon sheets due to plane growth and stacking of the carbon sheets and that the samples heated at lower temperatures have smaller carbon sheets and consequently can have higher SO₃H densities because the SO₃H groups are only attached to the edges of the carbon sheets (i.e., attached to phenolic OH groups).^[21] Therefore, a-CSS treated at 600 °C had a lower SO₃H density due to the low density of phenolic OH groups despite the much larger surface area. When a-CSS was employed to catalyze fructose into 5-HMF (Figure 4), it showed lower activity than CSS, which can be expected in view of the low SO₃H density of a-CSS. Since CSS had a higher catalytic activity for 5-HMF than that of a-CSS, CSS was used as the catalyst in further experiments.

Influence of catalyst concentration on 5-HMF yield

Figure 5 shows the effect of different amounts of catalyst CSS on 5-HMF yields. In the absence of catalyst, no 5-HMF was formed in 30 min at 80 °C. In the presence of CSS catalyst (0.01 g), a 5-HMF yield of 45 % was obtained after 20 min. After adding more catalyst (0.03 and 0.05 g), the 5-HMF yield increased to 62 and 77%, respectively, under the same reaction conditions. However, further increasing the amount of catalyst (0.1 g) resulted in a decrease in 5-HMF yield to 67% in 20 min; this may be attributed to excess acid-active sites that facilitate not only the dehydration of fructose into 5-HMF, but also the degradation of 5-HMF formed into other products, such as humins.^[22] At present, humins could not be quantified according to their composition, but their occurrence could be determined from the color change of the reaction mixtures into a deep brown color.^[14,23] Therefore, 0.05 g catalyst was selected as an appropriate amount for subsequent experiments.



Figure 5. Effect of catalyst concentration $[0 (\bullet), 0.01 (\odot), 0.03 (\bullet), 0.05 (\bullet),$ and 0.10 g (\triangleleft)] on fructose conversion into 5-HMF in [BMIM][CI] catalyzed by CSS. Reaction conditions: fructose (0.10 g), [BMIM][CI] (1 g), 80 °C.

Influence of reaction temperature on 5-HMF yield

The effect of the reaction temperature on fructose conversion into 5-HMF catalyzed by CSS in [BMIM][CI] was investigated (Figure 6). When the reaction was carried out at 70 °C, low re-



Figure 6. Effect of reaction temperature [70 (**u**), 80 ($_{\odot}$), 90 (**A**), and 100 °C (**•**)] on the yield of 5-HMF from fructose in [BMIM][CI] catalyzed by CSS. Reaction conditions: fructose (0.10 g), [BMIM][CI] (1 g), CSS (0.05 g).

action rates were observed and a yield of only 3% of 5-HMF was obtained in 10 min. The 5-HMF yield increased to 52% by allowing the reaction to proceed for 60 min. When the reaction temperature was elevated to 80 and 100 °C, reaction rates and 5-HMF yields increased in the initial stages of the reaction, and 5-HMF yields of 27 and 61% were obtained, respectively, for 3 min reaction time. However, higher reaction temperatures not only favored the dehydration of fructose into 5-HMF, but also accelerated the formation of humins; this is the primary factor that affects the yield of 5-HMF in acid-catalyzed reactions of carbohydrates in ionic liquids. Therefore, the yields of 5-HMF did not increase accordingly with increasing reaction temperatures for all reaction times studied. The highest 5-HMF

yield of 77% was obtained after 20 min at 80°C. We performed a control experiment to examine 5-HMF stability in the system by adding 5-HMF (0.1 g) and CSS (0.05 g) to [BMIM][Cl] (1 g) in the absence of fructose. After 30 min at 80°C, 98% of 5-HMF could be recovered, indicating that 5-HMF was stable under the experimental conditions in the absence of fructose and rehydration of 5-HMF into levulinic acid and formic acid could be suppressed in a nonaqueous ionic liquid system. Although the generation of humins seems to be inevitable in acid-catalyzed processing of carbohydrates, further investigations should be conducted to minimize its adverse effect on 5-HMF yield.

Effect of initial fructose concentration on 5-HMF yield

The tolerance of a catalytic reaction system to high feedstock concentrations is an important aspect to evaluate its efficiency and its potential for use in practical applications. In the acid-catalyzed dehydration of fructose, the 5-HMF molecules formed tend to combine with fructose molecules and cross-polymerize to generate humins. Thus, the initial fructose concentration has a large effect on the 5-HMF yield and selectivity, especially in aqueous or organic solvents.^[10,14,23] The influence of variations of initial fructose concentrations on 5-HMF yield for the reaction in [BMIM][CI] catalyzed by CSS was examined, and the results are shown in Table 2. The ratio of SO₃H groups in the catalyst to fructose amount was controlled, so that it decreased with increasing fructose loading.

It can be seen from the results given in Table 2 that the rate of 5-HMF formation from fructose decreased with increasing fructose concentration. For example, when fructose amounts of 0.01, 0.03, 0.1, and 0.2 g were used, the 5-HMF yields were

Table 2. Effect of fructose concentration on the dehydration of fructose into 5-HMF in [BMIM][CI] catalyzed by CSS catalysts. ^[a]								
Run	Initial fructose [g]	SO₃H/fructose [mmol/mmol]	Reaction time [min]	5-HMF yield [%]				
1	0.01	0.86	3	70				
2			5	72				
3			10	83				
4			20	74				
5	0.03	0.287	3	68				
6			5	69				
7			10	70				
8			20	73				
9			30	66				
10	0.10	0.086	3	27				
11			5	54				
12			10	63				
13			20	76				
14			30	76				
15	0.20	0.043	3	24				
16			5	29				
17			10	43				
18			20	47				
19			30	55				
20			60	67				
21			90	71				
[a] Rea	[a] Reaction conditions: [BMIM][Cl] (1 g), catalyst (0.05 g), 80 $^\circ\text{C}.$							

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4

83, 70, 63, and 43% after 10 min, respectively; this can be attributed to the decrease in the ratio of catalytic active sites $(SO_3H \text{ groups})$ in CSS to fructose concentration. However, with prolonged reaction times, high 5-HMF yields were obtained in all cases. For example, for the case of 0.2 g fructose being loaded, 71% of 5-HMF yield was obtained in 90 min reaction time. Therefore, the reaction with prepared CSS catalyst in an ionic liquid is applicable to high feedstock concentrations.

Recycling of CSS

To investigate the activity and stability of the CSS catalyst in the fructose-ionic liquid reaction system, recycling of the CSS catalyst was studied for five cycles (Figure 7). Experiments



Figure 7. Recycling of the catalytic system. Reaction conditions: fructose (0.10 g), [BMIM][CI] (1 g), CSS (0.05 g), 80 $^\circ$ C, 20 min.

were carried out at 80 °C for 20 min. The product 5-HMF was effectively separated from the solvent mixture after the reaction by extraction with ethyl acetate (8×6 mL), since [BMIM] [CI] and fructose were insoluble in ethyl acetate and 5-HMF was the sole product in the ethyl acetate phase, as noted by Hu et al.^[24] The number of mols of 5-HMF extracted with ethyl acetate was taken to represent the amount of 5-HMF formed during the reaction. After the extraction, the reaction mixture was heated at 60 °C for 24 h in a vacuum oven to remove water and residual ethyl acetate and then it was used directly in the next run by adding an equal amount of fresh fructose. It can be seen from Figure 7 that a 5-HMF yield of 77% was obtained for the first use of CSS catalyst and this only decreased slightly to 72% 5-HMF after five successive recycles. Residual humins or water-soluble products, if present in the reaction solvent, did not seem to have any significant effect on the yields obtained with the reaction solvents and recycled catalysts. Thus, the recycled catalytic system gave comparable 5-HMF yields; this indicated that the CSS catalyst retained good activity for the conversion of fructose into 5-HMF after repeated use.

Conclusions

Carbon materials prepared by incomplete hydrothermal carbonization of cellulose and post-treatment sulfonation or KOH activation resulted in highly active solid acid catalysts with -SO₃H, -COOH, and phenolic -OH groups. The catalysts were effective for the catalytic transformation of fructose into 5-HMF (5-hydroxymethylfurfural). With CSS (carbonaceous sulfonated solid), a 5-HMF yield of 83% could be obtained in [BMIM][Cl] (1-butyl-3-methylimidazolium chloride) at 80 °C for 10 min. Catalyst a-CSS (activated CSS) exhibited a somewhat lower activity than that of CSS, even though a-CSS had a much larger surface area than that of CSS. The lower activity of the a-CSS catalyst compared with that of the CSS catalyst can be attributed to the lower concentration of -SO₃H groups. The use of an ionic liquid with CSS resulted in the reaction being stable for five cycles and this combination could be applied to the conversion of high-concentration fructose solutions (ca. 20 wt%).

Experimental Section

Materials: Fructose (99%), sulfuric acid (99%), ethyl acetate, ethanol, and potassium hydroxide were used as received from Guangfu fine chemicals research institute (Tianjin). [BMIM][Cl] (99%) was obtained from Henan Lihua Pharmaceutical (Xinxiang). Microcrystal-line cellulose (pharmaceutical grade, ca. 50 μ m) was obtained from the Boya company (Tianjin), and 5-HMF (98%) was purchased from the Acros Organics company (Geel).

Preparation of carbonaceous solid acid catalysts: The cellulose-derived solid acid catalysts were prepared by hydrothermal treatment of cellulose and sulfonation according to the following two-step procedure. Typically, cellulose (6 g) was dispersed in water (50 mL) and the mixture was then transferred to a 100 mL stainless-steel autoclave and heated to 250 °C; conditions were maintained for 4 h at the autogenous pressure. The resulting carbonaceous solid materials were denoted CS.

The CS samples were recovered by centrifugation and washed with water and ethanol several times and dried at 80 °C for 12 h in a vacuum oven. The CS samples were then heated in concentrated sulfuric acid at 200 °C under a nitrogen atmosphere. After heating for 12 h and cooling to room temperature, the black precipitate was washed with distilled water until sulfate ion impurities could no longer be detected in the washings. The obtained sulfonated black materials were dried for 12 h at 80 °C and ground into powder. The resulting carbonaceous solid materials were denoted CSS.

To increase the specific surface area of the prepared carbonaceous solid acid catalyst, CS was chemically activated by using KOH before sulfonation. Briefly, the CS sample and KOH were mixed in a weight ratio of KOH/CS of 4 and then the mixture was heated to 600 °C under a flow of nitrogen and maintained under these conditions for 1 h. The samples were then thoroughly washed repeatedly with a 1 mol L⁻¹ aqueous solution of HCl to remove inorganic salts and washed with distilled water until a neutral pH of the washings was obtained. The wet solids were filtered to remove excess water and dried at 80 °C for 12 h. The dried solids were subjected to the sulfonation procedure described above. The sulfonated catalyst thus synthesized was denoted a-CSS.

Catalyst characterization: The catalysts were characterized by XRD (D/max-2500, RIGAKG), SEM (S4800, HITACHI), FTIR spectroscopy

(MAGNA-560, NICOLET), elemental analysis (Vario EL cube, Elementar), ICP (ICP-9000, Thermo Jarrell-Ash Corp., USA), and BET surface area techniques (ASAP2020, Micromeritics Instrument Corp, USA). FTIR spectra were obtained over the range from 400 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹. The BET surface area of the sample was calculated on the basis of nitrogen adsorption–desorption isotherms at -196 °C by a multipoint BET method.

Experimental procedure for reactions: In a typical experiment, fructose (0.1 g) was dissolved in [BMIM][Cl] (1 g) and then catalyst (0.05 g) was added. The reaction mixture was heated to 80 °C in a closed reactor with an oil bath, and conditions were maintained for a given reaction time. After the desired reaction time elapsed, the reactor was cooled to room temperature with a cold water bath within 1 min and water (0.5 g) was added to the reactor. 5-HMF was extracted from the reaction mixture with ethyl acetate. Products were measured with a Cary-50 Model spectrophotometer (Varian) at 284 nm by using the standard curve method. The yield of 5-HMF was calculated on a molar basis from Equation (1):

5-HMF yield (mol %) =
$$\frac{c(5\text{-HMF in product})}{c(\text{fructose in loaded sample})} \times 100\%$$
 (1)

in which c is the concentration. All results were replicated at least three times, and reproducibility of 5-HMF yields was within 4% standard deviation.

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- [1] A. Corma, S. Iborra, A. Velty, Chem. Rev. 2007, 107, 2411-2502.
- M. E. Zakrzewska, E. Bogel-Lukasik, R. Bogel-Lukasik, *Chem. Rev.* 2011, 111, 397–417; G. Yong, Y. G. Zhang, J. Y. Ying, *Angew. Chem.* 2008, 120, 9485–9488; *Angew. Chem. Int. Ed.* 2008, 47, 9345–9348; T. Støhlberg, W. J. Fu, J. M. Woodley, A. Riisager, *ChemSusChem* 2011, 4, 451–458.
- [3] F. Guo, Z. Fang, T. J. Zhou, Bioresour. Technol. 2012, 112, 313-318.

- [4] Z. H. Zhang, Q. A. Wang, H. B. Xie, W. J. Liu, Z. B. Zhao, *ChemSusChem* 2011, 4, 131–138; H. B. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, *Science* 2007, 316, 1597–1600.
- [5] Y. Román-Leshkov, J. N. Chheda, J. A. Dumesic, Science 2006, 312, 1933– 1937.
- [6] M. Bicker, J. Hirth, H. Vogel, Green Chem. 2003, 5, 280–284; Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, Nature 2007, 447, 982– U985.
- [7] J. N. Chheda, Y. Roman-Leshkov, J. A. Dumesic, Green Chem. 2007, 9, 342–350.
- [8] V. V. Ordomsky, J. van der Schaaf, J. C. Schouten, T. A. Nijhuis, J. Catal. 2012, 287, 68–75.
- Z. H. Zhang, B. Liu, Z. B. Zhao, *Carbohydr. Polym.* 2012, *88*, 891–895; Y. Yang, C. W. Hu, M. M. Abu-Omar, *Green Chem.* 2012, *14*, 509–513; B. R. Caes, R. T. Raines, *ChemSusChem* 2011, *4*, 353–356; B. Kim, J. Jeong, D. Lee, S. Kim, H. J. Yoon, Y. S. Lee, J. K. Cho, *Green Chem.* 2011, *13*, 1503–1506.
- [10] X. H. Qi, M. Watanabe, T. M. Aida, R. L. Smith, Green Chem. 2008, 10, 799–805.
- [11] X. H. Qi, M. Watanabe, T. M. Aida, R. L. Smith, ChemSusChem 2009, 2, 944–946.
- [12] C. Carlini, M. Giuttari, A. M. R. Galletti, G. Sbrana, T. Armaroli, G. Busca, *Appl. Catal. A* **1999**, *183*, 295–302; C. Carlini, P. Patrono, A. M. R. Galletti, G. Sbrana, *Appl. Catal. A* **2004**, *275*, 111–118.
- [13] X. H. Qi, M. Watanabe, T. M. Aida, R. L. Smith, Ind. Eng. Chem. Res. 2008, 47, 9234–9239.
- [14] B. F. M. Kuster, Starch/Staerke 1990, 42, 314-321.
- [15] M. Toda, A. Takagaki, M. Okamura, J. N. Kondo, S. Hayashi, K. Domen, M. Hara, *Nature* **2005**, *438*, 178–178.
- [16] S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi, M. Hara, J. Am. Chem. Soc. 2008, 130, 12787 – 12793.
- [17] F. Guo, Z. Fang, C. C. Xu, R. L. Smith, Jr., Prog. Energy Combust. Sci. 2012, 38, 672–690.
- [18] K. Fukuhara, K. Nakajima, M. Kitano, H. Kato, S. Hayashi, M. Hara, Chem-SusChem 2011, 4, 778-784.
- [19] X. M. Sun, Y. D. Li, Angew. Chem. 2004, 116, 607–611; Angew. Chem. Int. Ed. 2004, 43, 597–601.
- M. Sevilla, A. B. Fuertes, *Carbon* 2009, 47, 2281–2289; R. Demir-Cakan,
 N. Baccile, M. Antonietti, M. M. Titirici, *Chem. Mater.* 2009, 21, 484–490.
- [21] M. Okamura, A. Takagaki, M. Toda, J. N. Kondo, K. Domen, T. Tatsumi, M. Hara, S. Hayashi, *Chem. Mater.* **2006**, *18*, 3039–3045.
- [22] X. H. Qi, M. Watanabe, T. M. Aida, R. L. Smith, Green Chem. 2009, 11, 1327–1331; S. K. R. Patil, C. R. F. Lund, Energy Fuels 2011, 25, 4745– 4755.
- [23] X. H. Qi, M. Watanabe, T. M. Aida, R. L. Smith, ChemSusChem 2010, 3, 1071–1077.
- [24] S. Q. Hu, Z. F. Zhang, Y. X. Zhou, B. X. Han, H. L. Fan, W. J. Li, J. L. Song, Y. Xie, Green Chem. 2008, 10, 1280–1283.

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FULL PAPERS

Solid improvement: Cellulose-derived carbon catalysts with $-SO_3H$, -COOH, and phenolic -OH groups are used for the efficient catalytic conversion of fructose into 5-hydroxymethylfurfural in an ionic liquid (see picture).



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Acid-Catalyzed Dehydration of Fructose into 5-Hydroxymethylfurfural by Cellulose-Derived Amorphous Carbon