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Graphene Oxide Catalyzed Dehydration of Fructose into 5-Hydroxymethylfurfural with Isopropanol as Cosolvent

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The design of green heterogeneous catalysts for the efficient conversion of biomass into platform molecules is a key aim of sustainable chemistry. Graphene oxide prepared from Hummers oxidation of graphite was proven to be a green and efficient carbocatalyst for the dehydration of fructose into 5-hydroxymethylfurfural (HMF) in some three-carbon and four-carbon alcohol mediated solvent systems. HMF was obtained in up to 87 % yield in 90 vol % isopropanol-mediated DMSO solvent. Some control experiments and analytical data showed that a small number of sulfonic groups and abundance of oxygen-containing groups (alcohols, epoxides, carboxylates) have an important synergic effect in maintaining the high performance of graphene oxide.

There has been strong political and technical focus to obtain transportation fuels and platform chemicals from biomass resources, because the threats of fossil resource exhaustion and worldwide environmental problems are becoming more serious.[1] In this context, the production of furan compounds, especially 5-hydroxymethylfurfural (HMF), from the dehydration of carbohydrates is considered to have particularly high potential, as HMF can be selectively transformed into a variety of 2,5-disubstituted furan derivatives that can serve as promising alternatives for chemicals derived from petroleum.[2] There are many factors that have a remarkable influence on the yield of HMF during the dehydration of carbohydrates. Relative to other feedstocks, the production of HMF from fructose is much easier because of the fact that the fructofuranoic structure is more reactive to dehydration. Therefore, fructose has always been chosen as an ideal model substrate to evaluate the performance of catalytic systems for biomass conversion.[3]

Catalysts with either Brønsted or Lewis acid sites were proven to be capable of dehydrating fructose into HMF.[4] On the way to green and sustainable chemistry, it is of critical importance to make continuing efforts in searching for new catalysts that are nontoxic, sustainable, and of high activity for the conversion of renewable hydrocarbon sources.[1a, 2a, 5] The development of novel solid heterogeneous catalysts for the replacement of environmentally hazardous liquid Brønsted and Lewis acid catalysts is currently an active area of research.[3, 6] In this respect, catalysts developed from elemental carbon are of special interest, as they are not only made from an inexhaustible resource with environmental acceptability, but they also have tailorable physical and chemical properties that endow them with tunable catalytic performance for different reactions.[5a, 7] Graphene has been the focus of attention in carbocatalysis and nanoscience recently, for it can be used either as a support to immobilize active species or as a metal-free catalyst owing to its outstanding electrical, electrochemical, and mechanical properties.[7, 8] Graphene oxide (GO) primarily functions as a precursor to reduced graphene oxide, and it is rich in a variety of oxygen-containing functionalities (e.g., alcohols, epoxides, carboxylates, sulfate groups), which makes it a green solid acid catalyst. Dreyer et al. confirmed GO as a convenient carbocatalyst for hydration reactions.[9] Dhakshinamoorthy et al. demonstrated GO to be an efficient acid catalyst for the ring opening of epoxides and the acetalization of aldehydes.[10] Recently, we discovered that GO could be used as a facile catalyst for the etherification of HMF with ethanol to produce 5-ethoxymethylfurfural.[11]

Besides the design of novel catalysts, searching for green and economical solvent systems is another key point in biomass conversion. Various solvents including water,[4b, 6b, 12] ionic liquids,[13] and aprotic organic solvents, especially dimethyl sulfoxide (DMSO),[14] have been employed as reaction media in the dehydration of carbohydrates to HMF. However, all of these solvents suffer from some limitations that prevent practical applications. Water holds great advantages owing to its ecological superiority and technological convenience. Unfortunately, it is inefficient for HMF production as a result of the formation of an abundance of byproducts, including levulinic acid, formic acid, and humins. Ionic liquids are promising solvents with high selectivity in biomass conversion; however, they are not desirable for industrial-scale processes, as the cost is presently too high. DMSO has been discovered to be an effective solvent for HMF production from sugars. High yields (up to 100 %) of HMF have been obtained in DMSO,[15] but the separation of the product is quite difficult because the boiling point of

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DMSO is high (196 °C), which necessitates energy-intensive isolation procedures that cause serious loss of HMF. One of the possible solutions for mitigating the undesirable impact of DMSO processes is the use of green and cost-efficient cosolvents to substitute a reasonable amount of DMSO. For example, Qi et al. utilized 7:3 (w/w) acetone/DMSO solvent mixtures as a reaction medium for the dehydration of fructose to HMF, and they found the addition of acetone had little impact on the results.[14b] However, the capacity of acetone to dissolve sugars is very low, which limited its further substitution to DMSO. Recently, alcohol-mediated solvent systems were successfully applied in the production of HMF from sugars.[16] Alcohols, as easy-to-use solvents, not only have high solubility to sugars,[16c] but they also have a minimal impact on the environment.

On the basis of previous reports, we report herein that graphene oxide can be used as an efficient carbocatalyst and isopropanol can be used as a green cosolvent for the dehydration of fructose into HMF. GO used in the study was prepared by Hummers' method, which was based on the exhaustive oxidation of graphite under strongly acidic conditions followed by exfoliation of graphite oxide under ultrasonic conditions (a detailed procedure for the preparation of GO is available in the Supporting Information). The GO sample obtained by the traditional Hummers method was conveniently prepared and did not require any additional hazardous treatments.[10b,17] Isopropanol was found to be an outstanding cosolvent for the substitution of DMSO. Up to 90% (volume fraction) of DMSO was substituted by isopropanol without a significant decrease in the yield of HMF, which thus minimizes the undesirable impact of the DMSO process.

Table 1. Dehydration of fructose into HMF over GO under different conditions.[a]

Catalyst loading [mg]	Amount of *i*PrOH [vol%]	Amount of DMSO [vol%]	Fructose conversion[b] [%]	HMF selectivity[b] [%]	HMF yield [%]
8	0	100	100	93	93
8	20	80	100	90	90
8	50	50	100	89	89
8	90	10	98	89	87
8	95	5	97	73	71
8	100	0	92	46	42
0	90	10	87	54	47
5	90	10	97	84	82
10	90	10	99	86	85
20	90	10	100	78	78

[a] Reaction conditions: Fructose (0.5 mmol) with a specific amount of GO mixed in DMSO/isopropanol (2 mL) at 120 °C for 6 h. [b] Conversion and selectivity were determined by using HPLC. The product was confirmed by using an authentic sample and NMR spectroscopy.

Initially, the dehydration of fructose was performed in pure DMSO, which was discovered to be an efficient solvent for the production of HMF. In a typical procedure, fructose (90 mg, 0.5 mmol) was dissolved in DMSO (2 mL), and the mixture was heated at 120 °C for 6 h in the presence of GO (8 mg). After the reaction, the yield of HMF was found to be as high as 93%, which was in agreement with the literature.[14a,16b] Subsequently, isopropanol was gradually added and used as a partial substitution for DMSO. As listed in Table 1, the addition of isopropanol did not decrease the yield of HMF clearly, even if the content of isopropanol was increased to as high as 90 vol%. The HMF yield remained acceptable (71%) up to an isopropanol-for-DMSO substitution level of 95%. The main byproduct was found to be 5-isopropoxymethylfurfural (PMF), which was formed from etherification of HMF with isopropanol, and its yield increased as the ratio of isopropanol was increased. If 100% isopropanol was used as the solvent, the yield of HMF significantly dropped to approximately 42%. Additionally, PMF was formed in 9% yield in pure isopropanol, and a small amount of insoluble product, namely, humins, was also observed. All these results indicate that isopropanol can be used as an efficient cosolvent with DMSO for the dehydration of fructose. However, DMSO plays a very important role in the reaction. Addition of 5% DMSO significantly increased the yield of HMF from 42 to 71%. This result indicates that DMSO may act as a cocatalyst and not just as a cosolvent in this dehydration reaction. To verify this proposal, the reaction was performed in a 9:1 isopropanol/DMSO mixture without GO, and HMF was obtained in 47% yield. DMSO has an important positive effect on the reaction mainly because of the following several aspects. First, it facilitates the formation of the furanoid form of fructose, which can be easily dehydrated to HMF.[18] Second, DMSO can act as both an electron acceptor and an electron donator to improve the dehydration of the sugars.[3b] Third, DMSO can prevent the formation of byproducts such as levulinic acid and humins from HMF.[14a] Moreover, as a versatile polar aprotic solvent, DMSO can dissolve both polar and nonpolar compounds, which makes it an effective solvent for sugars and the products.

The catalytic performance of GO with different loadings was investigated. As mentioned above, it seems that the conversion of fructose into HMF can proceed with or without catalyst in isopropanol/DMSO solution, and the addition of an appropriate amount of GO can efficiently improve the yield of HMF. In the presence of GO (5 mg), HMF was obtained in 82% yield, and after adding more catalyst (i.e., 8 mg), the yield of HMF further increased to 87%. However, increasing the amount of GO to 10 mg caused a small decrease in the yield of HMF (85%), and a further increase in the catalyst loading to 20 mg resulted in a decrease in the yield of HMF to 78%. This result may be attributed to the high loadings of GO, which can not only promote the dehydration of fructose to HMF but also facilitate the degradation and polymerization of HMF to byproducts and humins. Notably, the formation of humins that could be absorbed on the surface of GO may cause serious catalyst deactivation.

Figure 1 shows the influence of reaction temperature and time on fructose dehydration to HMF catalyzed by GO. It was found that the reaction temperature was another important factor in the dehydration of fructose to HMF. The yield of HMF increased slowly to 68% at 100 °C after a reaction time of 6 h. Even if the reaction time was prolonged to 16 h, HMF was obtained in only approximately 78% yield. However, if the reac-

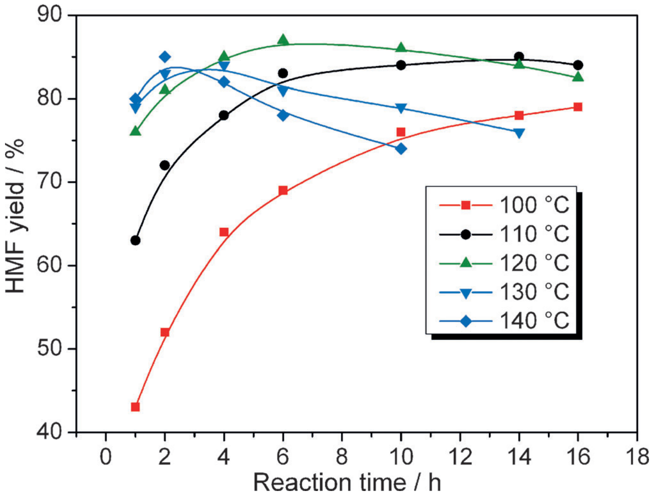

Figure 1. Effect of reaction temperature and time on the yield of HMF from the dehydration of fructose catalyzed by GO. Reaction conditions: fructose (90 mg), GO (8 mg), isopropanol (1.8 mL), DMSO (0.2 mL).

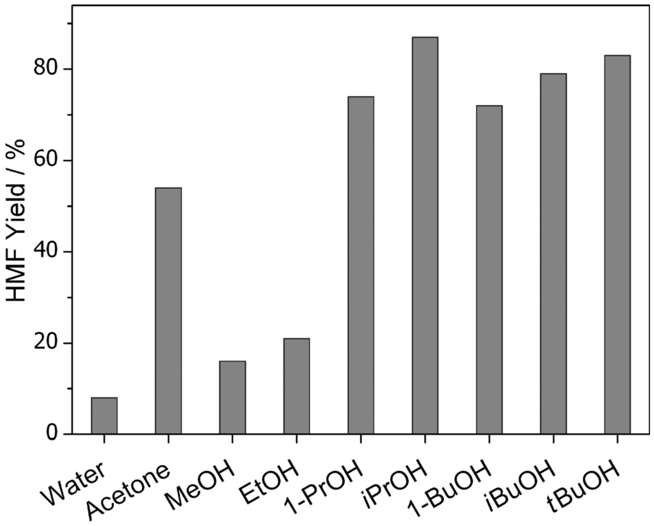

Figure 2. Effect of different solvents mixed with DMSO on the production of HMF from fructose catalyzed by GO. Reaction conditions: fructose (90 mg), GO (8 mg), solvent (1.8 mL), DMSO (0.2 mL), $T=120\,^{\circ}C$, $t=6$ h.

tion temperature was increased to 110 or 120 °C, HMF was obtained in 78 or 85% yield, respectively, within a reaction time of approximately 4 h, and this indicates that raising the reaction temperature efficiently improves the rate of fructose dehydration to HMF. However, higher reaction temperatures were not favorable for this reaction, as not only did this promote the dehydration of fructose, but it also accelerated the etherification reaction and the formation of humins, which thus decreased the yield of HMF. The maximum yield of HMF was 87%, which was achieved at 120 °C after a reaction time of 6 h. Further prolongation of the reaction at 120 °C led to a slight decrease in the yield of HMF. In addition, the stability of HMF in the solvent system without fructose was examined. In a control experiment, HMF (0.63 mg) and GO (0.8 mg) were added to a mixture of isopropanol (1.8 mL) and DMSO (0.2 mL) in the absence of fructose. After 6 h at 120 °C, 94% of HMF was recovered, and the main product was found to be PMF (no humins was found), which indicates that HMF was stable in the isopropanol/DMSO solvent system in the absence of fructose. The formation of humins and rehydration products such as levulinic acid and formic acid could be suppressed effectively.

Afterwards, several different solvents were tested as the cosolvent with DMSO for the production of HMF under the optimized reaction conditions. As it can be seen in Figure 2, water was not an effective cosolvent, as it gave HMF in a low 8% yield, and this is probably because water can induce serious side reactions such as the rehydration and polymerization of HMF. In addition, water is another main product in the dehydration reaction; thus, it is not favorable to shift the equilibrium towards the production of HMF. Acetone, an environmentally friendly solvent with a molecular structure similar to that of DMSO, was also tested as the cosolvent in the reaction, and a moderate yield of HMF (54%) was obtained. Nearly complete conversion of fructose was found upon using methanol and ethanol as the cosolvents; however, the yield of HMF was much low than that obtained with the use of isopropanol. The low selectivities towards HMF in methanol and ethanol are attributed to the formation of HMF–alcohol ether products, as the reaction conditions are also suitable for the etherification reaction, and these results are in accordance with previous studies.[11,16c,19] Upon using 1-propanol, isopropanol, 1-butanol, isobutanol, and *tert*-butanol as cosolvents, the yield of HMF was significantly higher than that obtained with the use of methanol and ethanol. The high selectivities towards HMF in these alcohols are probably due to their bulkiness and steric hindrance, which can reduce the activity of the etherification reaction. The highest yield of HMF was obtained upon using isopropanol as the cosolvent, and this is likely related to the higher solubility of fructose in this solvent and its lower etherification reactivity with HMF.

Subsequently, the active sites present in GO were assessed by some control experiments. Initially, glacial acetic acid, *p*-toluenesulfonic acid, concentrated sulfuric acid, and Amberlyst-15 were used as catalysts in their optimum amounts under similar conditions (see Table S1, Supporting Information). It was found that all of the acidic catalysts could facilely promote the dehydration reaction except glacial acetic acid, which indicates that the active sites of GO are probably the sulfonic groups rather than the carboxylic groups. It was also found that, with their optimum loadings, the yield of HMF (87%) was clearly higher if GO was used as the catalyst instead of Amberlyst-15 (HMF yield of 71%). The difference in the two is that GO contains a diverse array of oxygen-containing groups, such as hydroxy, epoxy, and carboxyl groups, as detected by FTIR spectroscopy (see Figure S1), whereas Amberlyst-15 contains sulfonic groups only. Thus, it can be deduced that other oxygen-containing functionalities on the surface of GO play an important role in the dehydration of fructose into HMF. To obtain an explanation for this phenomenon, affinities of different catalysts to fructose and HMF were evaluated by adsorption experiments. It was discovered that the adsorption of fructose on GO was much higher than that on Amberlyst-15 (see Table S2). The higher affinity of GO to fructose should be due to the presence of the surface oxygen-containing groups, which can form strong hydrogen-bonding interactions with the hydroxy groups existing in fructose. Moreover, a larger amount of ether product was formed if Amberlyst-15 was used as the catalyst, and this is probably due to its stronger acidity. Therefore, it could be concluded that GO has appropriate acidity and strong adsorption towards fructose, and these factors may account for its higher catalytic performance.

To further detect the acid sites on GO and assess the thermal stability of these active sites, GO was thermally treated at different temperatures and was characterized by diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) and thermogravimetry/mass spectrometry (TG–MS). It is known that heat treatment of GO can result in the removal of some oxygen-containing groups to reconstitute graphene.[20] TG analysis of GO showed that there were two main stages of mass loss (see Figure S2). The mass loss at approximately 100 °C corresponds to partial interlayer water and surface-adsorbed water of GO. The large mass loss at approximately 210 °C is attributed to the loss of the abundant oxygen-containing groups. Notably, the loss of sulfur content was not clear, even at a temperature of 220 °C, as indicated by MS.

On the basis of the results of TG–MS analysis, DRIFT was applied to monitor the changes in the acid sites of GO after treatment at different temperatures. The bands at approximately 3600 cm^{-1} are attributed to O–H stretching.[21] The bands at 3280, 3010, and 2860 cm^{-1} can be assigned to NH_4^+, which is formed by the reaction of NH_3 with some Brønsted acid sites on GO. The band at 1780 cm^{-1} is attributed to NH_3 coordinated to the Lewis acid sites on GO. The three bands in the range from 1480 to 1660 cm^{-1} are ascribed to some synthetic factors, including amide stretching and ammonium bending.[22] As depicted in Figure 3, at relatively low temperature treatments (below 150 °C), the main acid sites of GO remain stable. However, if GO was treated above 200 °C, some Brønsted acid sites disappeared rapidly. At a temperature of 215 °C, almost all of the signals between 2500 and 3600 cm^{-1} disappeared. These results are consistent with the results of TG–MS, as GO is unstable above 200 °C; most of the oxygen-containing groups that account for the majority of the acid sites are removed. However, the sulfate groups on GO are still stable even after heat treatment at 215 °C, as indicated in Figure 3 (1050 to 1150 cm^{-1}). Moreover, after heat treatment at different temperatures GO was used as a catalyst for the reaction (see Table S3). It was found that the catalytic activity declined rapidly after GO was treated above 200 °C, and it remained almost unchanged if GO was treated below 150 °C. Thus, this once again suggests that the oxygen-containing groups on GO play a very important role in maintaining the high catalytic activity of GO for the fructose dehydration reaction.

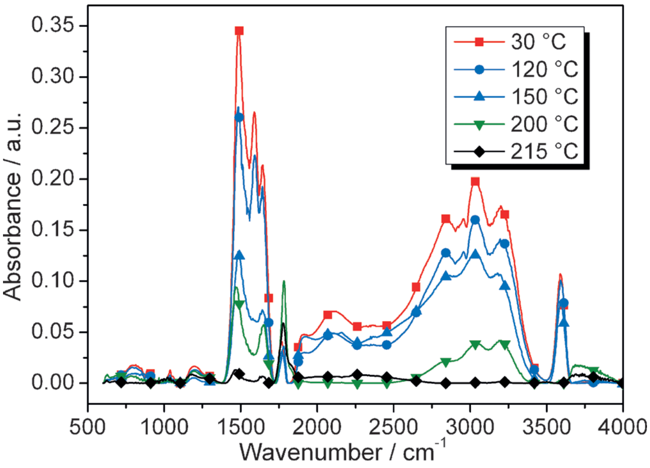

Figure 3. DRIFT spectra of NH_3-adsorbed GO after thermal treatment at different temperatures.

Finally, the reusability of GO was investigated (see Figure S4). It was observed that the catalytic activity of GO dropped slightly after four runs, which is similar to a previous report.[11] This result was mainly due to the loss of some oxygen-containing groups during the long thermal treatment. However, it is easy to recover the full catalytic activity of GO by handling the reused GO under the conditions of Hummers' method (see Figure S4).

In conclusion, graphene oxide prepared by Hummers' method was used as an efficient carbocatalyst for the dehydration of fructose into HMF in some three-carbon and four-carbon alcohol mediated solvent systems. These alcohols can be used as green cosolvents for the partial substitution of DMSO to minimize its negative effects. The highest yield of HMF (87%) was obtained with the use of 90 vol% isopropanol as the cosolvent. Both the reaction temperature and the loading of GO had a remarkable influence on the yield of HMF. In addition, some control experiments and analytical data showed that a small number of sulfonic groups should account for the active sites, whereas an abundance of oxygen-containing groups (alcohols, epoxides, carboxylates), which can form strong hydrogen-bonding interactions with fructose, have an important synergic effect in maintaining the high performance of GO. Moreover, GO was found to be stable after heat treatment below 150 °C, whereas most of the oxygen-containing groups were removed upon treatment above 210 °C. Given that GO can be readily functionalized, it is envisaged that many more new carbocatalysts with engineered morphology or functionality will emerge and play an important role in green and sustainable chemistry in the near future.

Experimental Section

Materials

Fructose (99%) and HMF (99%) were purchased from Amresco and J&K Scientific Company, respectively. Graphite powder was purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). DMSO, 1-propanol, isopropanol, 1-butanol, and all other chemicals (analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All reagents were used as received without further purification.

Preparation of GO

Typically, graphite powder (8000 mesh, 5 g) suspended in sulfuric acid (115 mL, 98 wt %) was oxidized by the addition of $NaNO_3$ (2.5 g), $KMnO_4$ (15 g), and H_2O_2 (30 wt %, 50 mL) in sequence. After that, the mixture was washed by HCl (1 м, 1 L) and a large amount of distilled water. Then, the graphite oxide suspension was ultrasonicated to form graphene oxide. Finally, the GO suspension was dried to obtain the GO powder. More detailed procedures and the characterization data are available in the Supporting Information.

Experimental procedure for reactions

In a typical experiment, fructose (90 mg), GO (8 mg), isopropanol (1.8 mL), and DMSO (0.2 mL) were charged in a 10 mL stainless app:ds:steel microautoclave with a Teflon lining and sealed by a screw cap. The autoclave was then heated to 120 °C and maintained at 120 °C for 6 h. The autoclave was fitted with a magnet stir bar and filled with air under ambient pressure. After the reaction, the autoclave was cooled to room temperature and GO was separated by filtration. The reaction mixture was diluted with 95 % ethanol and filtered with a 0.45 μm syringe filter prior to analysis. The yield of HMF was determined by using a Shimadzu high-pressure liquid chromatograph (LC-10AT) equipped with a UV detector and an evaporative light-scattering detector. A 4.6 mm id × 250 mm Kromstar C18 reverse-phase column was used. The mobile phase consisted of deionized water and acetonitrile with a volume ratio of 7:3 at a flow rate of 0.6 $mL\,min^{-1}$. For the analysis of fructose, a 4.6 mm × 250 mm Shodex sugar column (SC1011) was used, and distilled water was used as the mobile phase at a flow rate of 1.0 $mL\,min^{-1}$. The column temperature was maintained at 35 °C. The yield of HMF and the conversion of fructose were calculated on the basis of external standard curves constructed with authentic standards.

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