Green Chemistry

COMMUNICATION

Graphene oxide as a facile acid catalyst for the one-pot conversion of carbohydrates into 5-ethoxymethylfurfural†

Hongliang Wang,[a,b] Tiansheng Deng,[a] Yingxiong Wang,[a] Xiaojing Cui,[a,c] Yongqin Qi,[a] Xindong Mu,[d] Xianglin Hou*[a] and Yulei Zhu*[a,c]

Graphene oxide obtained by the Hummers method was discovered to be an efficient and recyclable acid catalyst for the conversion of fructose-based biopolymers into 5-ethoxymethylfurfural (EMF). EMF yields of 92%, 71%, 34% and 66% were achieved when 5-hydroxymethylfurfural (HMF), fructose, sucrose and inulin were used as starting materials, respectively.

Diminishing fossil reserves and environmental problems necessitate the development of processes using sustainable, green, and environmentally benign resources for the production of fuels and bulk chemicals.[1–3] As a widely available and sustainable carbon source, biomass has the potential to replace current non-renewable fossil resources.[4] It was predicted by the roadmap for Biomass Technologies in the U.S. that 18% of all manufactured chemicals will originate from biomass by 2020.[5] The boom in the chemical industry based on biomass demands the development of green and economical technologies for the efficient conversion of biomass into important platform molecules, as well as ways for converting these platform molecules into various base chemicals.[6,7]

5-Hydroxymethylfurfural (HMF), produced from carbohydrates such as fructose, glucose, sucrose, inulin and even cellulose, has been envisaged as one of the top building block chemicals in biorefinery processes.[8–11] It can be transformed into a number of important compounds with a high potential to be used in fuel or polymer applications, including furan derivatives such as 2,5-furandicarboxylic acid, 2,5-diformylfuran, 2,5-bishydroxymethylfuran, 2,5-dimethylfuran, and non-furanic compounds such as levulinic acid, 1,6-hexanediol,

adipic acid, caprolactam, and caprolactone.[4,12–14] 5-Ethoxymethylfurfural (EMF), synthesized by etherification of HMF with ethanol, has recently attracted much attention as a potential biofuel alternative.[15–18] The energy density of EMF is 30.3 MJ L^{-1}, which is 29% greater than that of ethanol (23.5 MJ L^{-1}) and very close to that of diesel (33.6 MJ L^{-1}).[19] EMF has generated positive results with a significant reduction of soot and SO_X emissions in engine tests.[19] Heteropolyacids, H-form zeolites, mesoporous silica, ion exchange resins, and a hybrid solid catalyst of $[MIMBS]_3PW_{12}O_{40}$ have been used for the synthesis of EMF from both HMF and fructose in ethanol.[15–18] Acceptable yields of EMF have been obtained when HMF was used as the starting material, while it is still troublesome to achieve high yields of EMF directly from fructose or other cheaper biopolymers by a one-pot process.

Carbon nanomaterials hold promise in the development of sustainable catalysts for green chemistry with low emissions and high selectivity.[20,21] Graphene-based materials in the growing field of "carbocatalysis" have become important in recent years due to their unique chemical properties, high mechanical resistance, and their propitiousness charge generation and transportation in catalytic processes.[21] Graphene oxide (GO) has functioned primarily as a precursor in the large-scale production of graphene. One of the most widely applied ways for the preparation of GO is the Hummers method, which is based on the exhaustive oxidation of graphite under strong acidic conditions (in concentrated sulfuric acid) by using permanganate and hydrogen peroxide.[22] A variety of oxygen-containing functionalities (alcohols, epoxides, and carboxylates) as well as a small quantity of sulfate groups were introduced to the graphene plane during the synthesis of GO under these harsh conditions. These extrinsic functional groups make GO an excellent catalyst for various synthetic transformations. GO has been reported to be a powerful catalyst in the oxidation of benzylic alcohols, unsaturated hydrocarbons, sulfides and thiols.[23–25] In addition, GO obtained by the conventional Hummers method was reported to be a highly efficient, recyclable acid catalyst for the ring opening of epoxides.[26]

[a]*Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, PR China. E-mail: houxl@sxicc.ac.cn, zhuyulei@sxicc.ac.cn; Fax: (+86) 351-4041153*
[b]*University of Chinese Academy of Sciences, Beijing, 100049, PR China*
[c]*State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, PR China*
[d]*Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, Shandong 266101, P. R. China*
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Intrigued by these previous studies, we were interested in examining whether GO, a readily available and inexpensive material, can be used as an efficient carbon catalyst for the transformation of renewable carbon sources into useful chemicals. GO obtained directly by the Hummers method without any further treatment was used, since it could not only be conveniently prepared, but also contains lots of recoverable Brønsted acid sites. Typically, graphite powder (8000 mesh, 5 g), suspended in sulfuric acid (115 mL, 98 wt%), was oxidized by $NaNO_3$ (2.5 g), $KMnO_4$ (15 g) and H_2O_2 (50 mL, 30 wt%) in sequence. After that, it was washed by HCl (1 L, 1 mol L^{-1}) 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. The detailed procedure of GO preparation is available in the ESI.† The performance of GO as an acid catalyst was tested for the conversion of carbohydrates into EMF, including the hydrolysis of biopolymers to form fructose, dehydration of fructose to form HMF, and etherification of HMF to form EMF (Scheme 1). It is known that all the aforementioned reactions (hydrolysis, dehydration and etherification) are readily promoted by acid catalysts.

In an optimized experiment, 0.5 mmol (63 mg) HMF was placed in a 5 mL micro autoclave, dissolved in 1 mL ethanol, and then heated to 100 °C in the presence of 20 mg GO for 12 h. After the reaction, the GO was removed by filtration. It was found that HMF had been transformed into EMF with a yield of 92% and a conversion of 96%, as determined by NMR and LC/MS. During the reaction, some active sites on the GO surface may dissolve into the solution, and these leached species may act as new active sites. To rule out this possibility, the reaction was first carried out with GO under the same conditions for 6 h, and then GO was removed from the reaction mixture by filtration. An EMF yield of 74% was achieved. The solution in the absence of GO was continued to stir at 100 °C for another 6 h, and no further HMF conversion and product formation were observed. These results indicate that the catalysis indeed occurs on the surface of GO, and that GO is a truly heterogeneous catalyst. Furthermore, when GO was replaced by natural flake graphite (used as the starting material to prepare GO) or the reduced graphene oxide (R-GO, the oxygen-containing functionalities and sulfate groups were removed by thermal treatment at 400 °C) under the same reaction conditions, no reaction was observed. This result reveals that the extrinsic functional groups on GO play a vital role in the catalytic etherification of HMF with ethanol.
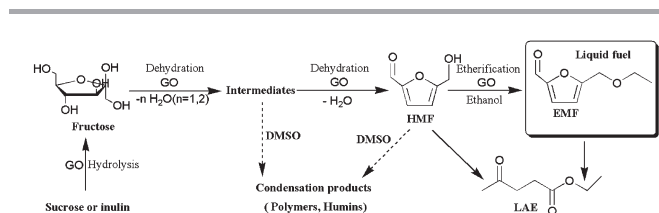
To evaluate the catalytic performance of GO, various other common acid catalysts were used under identical reaction conditions, and the results are summarized in Table 1. Homogeneous acids such as H_2SO_4, p-toluenesulfonic acid (p-TSA) and $H_3PW_{12}O_{40}$ were tested in the reaction, and yields of EMF were 54%, 61% and 82% with complete conversion of HMF, respectively. These results are consistent with those of previous studies.[15,17] The main by-product was detected to be ethyl levulinate (LAE). Moderate yields of EMF with high conversions of HMF were achieved by using H_2SO_4 and p-TSA, probably due to the strong acidity of the two catalysts, which could give rise to ring-opening alcoholysis of HMF and thus lead to the formation of ethyl levulinate. A relatively high yield of EMF was obtained when $H_3PW_{12}O_{40}$ was used as the catalyst. However, it was dissolved in the reaction mixture, making separation and recycling difficult. Amberlyst-15, a widely used heterogeneous acid catalyst, was also subjected to this reaction, and it was found that the yield of EMF as well as the conversion of HMF were similar to those of the H_2SO_4-catalysed reaction. As listed in Table 1, among all the screened catalysts, GO exhibited the highest yield of up to 92% with a HMF conversion of 96% when the catalyst loading was 20 mg, indicating that GO is an excellent acid catalyst for this reaction. Furthermore, the effect of the GO loading on the catalytic performance was explored. The yield of EMF was decreased to 83% at a low HMF conversion of 85% when the GO loading was reduced to 10 mg. An increase in catalyst loading from 20 mg to 30 mg resulted in a slight improvement of the HMF conversion; however, this caused a decrease in the EMF yield. Increasing of the GO loading to 40 mg resulted in a further decrease of the EMF yield. The promotion of side reactions including the alcoholysis of HMF to LAE and the formation of insoluble products was observed during the increase of GO loading. Thus, a low catalyst loading resulted in a low HMF conversion that led to a low EMF yield; a high catalyst loading resulted in a high HMF conversion but may have also induced side reactions that led to a low EMF yield. Therefore, a suitable amount of catalyst

Table 1 Etherification of HMF with ethanol into EMF over GO and other catalysts[a]

Entry	Catalyst	Loading	HMF conversion (%)	EMF yield (%)
1	GO	20 mg	96	92
2[b]	Graphite	20 mg	—	—
3[c]	R-GO	20 mg	—	—
4	H_2SO_4	3 mol%	100	54
5	p-TSA	3 mol%	100	61
6	$H_3PW_{12}O_{40}$	5 mol%	100	82
7	Amberlyst-15	10 mg	99	59
8	GO	10 mg	85	83
9	GO	30 mg	99	89
10	GO	40 mg	99	85

[a] Reaction conditions: 0.5 mmol HMF with the specific catalyst was mixed in 1 mL ethanol and reacted at 100 °C for 12 h. [b] Natural flake graphite was purchased from Sinopharm Chemical Reagent Co. Ltd, China and used without further purification. [c] Reduced graphene oxide was prepared by thermal treatment at 400 °C.

Scheme 1 The conversion of carbohydrates to EMF catalyzed by GO.

should be added, and 20 mg GO was proved to be the best for the present reaction system.

The effects of the reaction temperature and reaction time on the etherification of HMF were also studied (Fig. 1). After reaction at the low temperature of 80 °C for 12 h, the yield of EMF was only 68%. When the reaction time was prolonged to 20 h, the EMF yield only increased slightly to 80%. However, it significantly increased to 92% by raising the reaction temperature to 100 °C for 12 h, indicating that high temperatures enhance the rate of HMF conversion. Further, when the reaction was carried out at 120 °C, the EMF yields were obviously higher than those at 100 °C in the initial 8 h, and the maximum yield of 85% was obtained within 7 h. In order to better understand the effect of the temperature on the etherification of HMF to EMF, we have constructed the kinetic profiles at different temperatures and calculated the activation energy. The detailed calculation method is described in the ESI.† The value of k (the rate constant for HMF conversion) increased from 1.07 h^{-1} to 0.219 h^{-1} and 0.418 h^{-1} when the temperature increased from 80 °C to 100 °C and 120 °C, respectively. Based on the rate constants we obtained, the activation energy (E_a) was calculated by the Arrhenius equation, and the apparent activation energy of the catalytic system was about 39.93 kJ mol^{-1}. Thus, it could be confirmed that the temperature has a positive effect on promoting this reaction – the higher the reaction temperature, the higher the etherification rate. However, HMF is unstable at high temperatures since it can be readily

transformed into LAE and humins by alcoholysis and polymerization. This leads to a low yield of EMF as shown in Fig. 1.

HMF can be obtained by dehydration of carbohydrates, especially readily from fructose, by using acid catalysts which are similar to those used in the aforementioned etherification reaction. Thus, the one-pot synthesis of EMF from low-cost carbohydrates was investigated in this work, and the results are listed in Table 2. Initially, fructose was used as the substrate in the reaction. The main products detected were HMF and EMF with yields of 9% and 18%, respectively, when fructose instead of HMF was used as the starting material in the reaction under conditions similar to those used for the etherification reaction (Table 2, entry 1). The total yield of the furan products was much lower (27%) compared to the high conversion of fructose (95%). LAE was detected, but its yield was low, too. Moreover, a small amount of brownish black humins was observed. The low selectivity towards furans in the reaction at 100 °C may be rooted in two aspects. One is that there may exist an abundancy of partially dehydrated intermediates generated in the process of fructose dehydration to HMF at low reaction temperatures (<130 °C), and the other is that side reactions such as the polymerization of these intermediates and alcoholysis of HMF have occurred in ethanol.[27] In our previous studies,[16] it was found that adding a certain volume of DMSO (dimethylsulfoxide) into ethanol could efficiently improve the yields of the furan products without causing much trouble in the product separation. Thus, 0.3 mL DMSO mixed with 0.7 mL ethanol was used as the reaction solution. The yield of HMF was significantly enhanced when DMSO was introduced (Table 2, entry 2), indicating that DMSO plays a positive role in the promotion of converting the dehydrated intermediates into HMF.

Subsequently, the effects of the reaction temperature and catalyst loading on the performance of GO were investigated in DMSO–ethanol solution. The total yield of the furan products increased from 54% to 78% when the temperature was increased from 100 °C to 130 °C. These results reveal that the dehydration of fructose requires higher temperatures than the
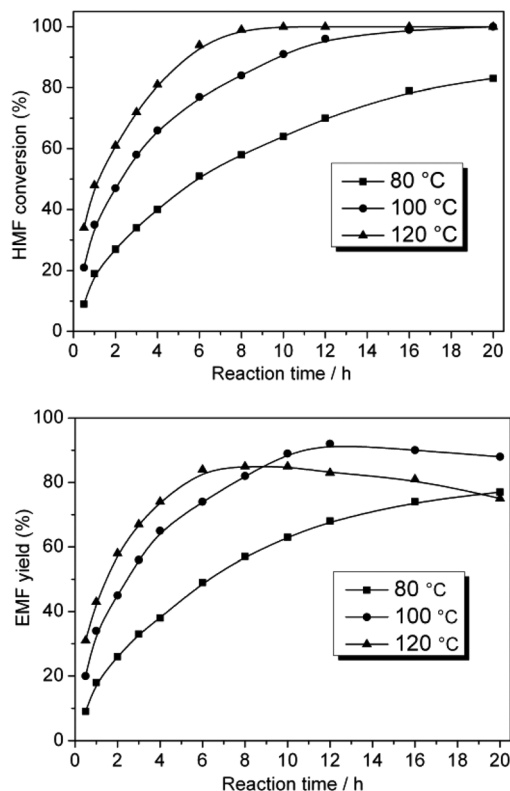

Fig. 1 Effects of reaction temperature and reaction time on the conversion of HMF to EMF. Reaction conditions: 0.5 mmol HMF, 20 mg GO, 1 mL ethanol.

Table 2 Production of EMF from various carbohydrates over GO under different conditions[a]

Entry	Substrate	T (°C)	Cat. loading (mg)	Substrate conversion (%)	HMF yield (%)	EMF yield (%)
1[b]	Fructose	100	20	95	9	18
2	Fructose	100	20	98	31	23
3	Fructose	130	20	100	14	64
4	Fructose	130	30	100	9	71
5	Fructose	150	30	100	3	62
6	Fructose	130	40	100	6	67
7	Sucrose	130	30	100	4	34
8	Inulin	130	30	100	7	66
9	Glucose	130	30	99	1	3

[a] Reaction conditions: 0.5 mmol carbohydrate based on the monosaccharide with a specific amount of GO mixed in 0.7 mL ethanol and 0.3 mL DMSO reacted for 24 h. [b] 0.5 mmol fructose with GO mixed in 1 mL ethanol and reacted at 100 °C for 24 h.
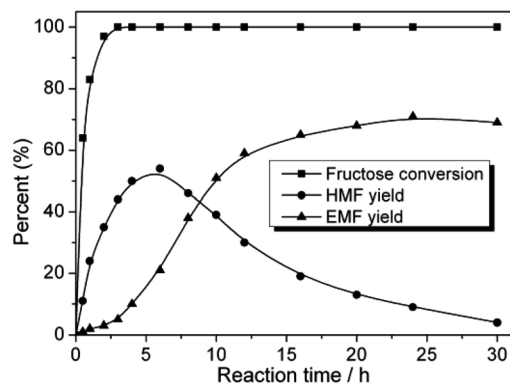
Fig. 2 Fructose conversion and product distribution as a function of the time over the GO catalyst. Reaction conditions: 0.5 mmol fructose, 30 mg GO, 0.3 mL DMSO, 0.7 mL ethanol, T = 130 °C.

etherification of HMF. The yield of EMF was further improved when the GO loading was increased to 30 mg. However, a further increase of the reaction temperature or the GO loading resulted in a drop in the furan product yield, since side reactions were promoted by the high temperature or over-active acid sites. Moreover, the conversion of fructose and the formation of the products as functions of the reaction time were carefully studied. As depicted in Fig. 2, a complete fructose conversion was achieved within 2 h. In the initial stage of the reaction, HMF was observed with a maximum yield of 54% at about 6 h, and after that it decreased gradually. Meanwhile, the yield towards EMF gradually increased to a maximum of 71% at about 24 h. This behaviour supports that the conversion of fructose in an ethanol–DMSO system is a typical consecutive reaction, and HMF is an intermediate in EMF production from fructose.

Next, the fructose based disaccharide (sucrose) and polysaccharide (inulin) were tested as the starting materials of the GO catalysis reaction. Sucrose is the most abundant and cheapest disaccharide, and one molecule of sucrose contains one glucose and one fructose unit. No sucrose was detected after the reaction; a 4% yield of HMF was obtained, and a 34% yield of EMF were obtained. When glucose was subjected to this reaction, the conversion was high (99%); however, the total furan product yield was low (4%). The major product was found to be ethyl glucoside. The results suggest that only the fructose unit in sucrose can be converted into HMF and EMF, and GO cannot be used as the catalyst for the isomerization of glucose to fructose. A much higher EMF yield (66%) was obtained when inulin was used as the substrate for the reaction. This result may be due to the fact that one molecule of inulin contains one glucose unit and 1–59 fructose units.[28] All these results indicate that GO can not only catalyze etherification and dehydration reactions, but also hydrolysis. Thus, GO can be used as a facile and efficient acid catalyst for the one step conversion of abundant and cheaper fructose-based carbohydrates into the promising biofuel EMF.

Finally, the reusability and stability of GO was investigated for the one-step conversion of fructose into EMF in a DMSO–ethanol solvent system under conditions identical to those described in Fig. 2. After the reaction, the solid GO was separated from the reaction mixture by filtration, and washed with 95% ethanol and then acetone three times each. Then, the washed GO was dried in an oven at 60 °C for 12 h. It was found that the activity of the catalyst for the conversion of fructose to EMF dropped slightly, but not obviously after four consecutive reuses (Fig. S1, ESI†). This might be due to the fact that GO undergoes partial thermal reduction (some oxygen-containing functionalities were lost under thermal treatment) during long term exposure to high temperatures.[29] The partial thermal reduction may lead to a minor decrease in the acid strength of GO, and this was supported by Infrared Fourier Transform spectroscopy (FT-IR) (Fig. S3, ESI†) and ammonia adsorption Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFT) (Fig. S4, ESI†). However, it is not troublesome to handle the partial thermal reduced GO under the Hummers method conditions to recover the full catalytic activity of the catalyst.

Conclusions

In conclusion, we have discovered that GO synthesized by Hummers oxidation of graphite can be used as a facile acid catalyst for the one-step conversion of fructose-based carbohydrates into high-heating value liquid biofuels. GO showed an excellent catalytic activity for the etherification of HMF in ethanol with a high EMF yield of 92%. GO also performed well in the one-pot conversion of fructose, sucrose and inulin in a DMSO–ethanol solvent system to obtain EMF with yields of 71%, 34% and 66%, respectively. The reaction temperature and catalyst loading had a notable effect on the EMF yield. Compared with the etherification reaction, the hydrolysis and dehydration reactions needed higher reaction temperatures and catalyst loading. Finally, GO can be reused several times without much loss in catalytic activity. Given the fact that the production of GO is now being scaled up industrially, it may open up a new way to apply GO in the catalytic conversion of biomass-based compounds into value-added chemicals, and open a new route in green and sustainable industry.

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