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Conversion of Glucose to Valuable Platform Chemicals over Graphene Solid Acid Catalyst

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Biomass-derived hexose sugars, the most abundant renewable resources in the world, have potential to be the sustainable resources for production of platform chemicals. Here, conversion of glucose is investigated by using sulfonated graphene (rGO-SO$_3$H) as solid acid catalyst in water without any organic solvent. At first, graphene functionalized with sulfonic acid groups is prepared by using NaH and propane sultone, and then it is characterized by means of XPS, FT-IR, and TEM to confirm the existence of the sulfonic acid groups. The catalytic activity of rGO-SO$_3$H in the conversion of glucose to valuable chemicals is studied under different reaction conditions. The maximum yield of 5-hydroxymethylfurfural (HMF) is 28.8%, and the total yield of formic acid, lactic acid and HMF is 51.94% when the reaction is conducted at the optimized reaction condition. In addition, the rGO-SO$_3$H gives a relatively high total yield of the three kinds of products after five run experiments, indicating that the catalyst shows good thermal stability.

Key words: Glucose, Graphene, Solid acid, Catalyst

I. INTRODUCTION

It is well known that the world is facing an energy crisis because of the shortage of non-renewable fossil resources which have been widely used to satisfy the global energy needs [1]. Non-renewable fossil resource decreased sharply in the past several decades. In order to solve this problem, it is necessary to make use of renewable biomass resources in the future. The renewable biomass resources are regarded as a potential alternative to non-renewable natural resources for sustainable production of fuels and chemicals [2]. Glucose is considered as the most abundant monosaccharide of promising biomass resource, which can be obtained from cellulose by different reaction system such as enzymes, dilute acids, and supercritical water. In addition, degradation of glucose has attracted much attention because glucose can be converted efficiently into various highly valuable platform chemicals such as 5-hydroxymethylfurfural (HMF), lactic acid, and formic acid [3]. HMF is a furan derivative containing hydroxylmethyl group and aldehyde groups, which can be used for synthesis of a variety of plastics, and other fine chemicals [4−7]. The chemical conversion of glucose to value-added platform chemicals using various catalysts and different reaction solvents has been investigated by

many researchers [8]. Recently, researchers have reported the synthesis of levulinic acid and HMF from glucose using dilute mineral acid such as HCl, H$_2$SO$_4$ and H$_3$PO$_4$ as catalyst [9]. Even though the total yield of levulinic acid and HMF is more than 50%, but the process has some disadvantages such as the difficulty of the separation of catalyst, corrosion to the equipments, and pollution to the environment. Ionic liquid has been widely used to convert glucose to useful products, which shows high catalytic activity, but the ionic liquid is high-cost and it is difficult to recover from the reaction system [10]. So a new heterogeneous catalyst should be developed to overcome the negative factor during the reaction.

Graphene has been widely used in many reactions for preparation of catalyst owing to its some advantages such as large surface area, excellent mechanical properties, and good conductivity [11]. Various kinds of graphene-based materials have been synthesized for different reactions such as degradation of biomass resources, investigation of its electrochemical performance and photocatalysis [12]. There are several reports on the preparation of sulfonic acid-functionalized graphene using chlorosulfonic acid, *p*-aminobenzenesulfonic acid and fuming sulfuric acid as sulfonated reagent [6, 13−15].

Here, the sulfonated graphene (rGO-SO$_3$H) as a new solid-acid catalyst was prepared and used for catalytic conversion of glucose to valuable platform chemicals. Different measurements were used to confirm the formation of sulfonated graphene at first, and then the ex-

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230

periment of conversion of glucose were preceded under hydrothermal conditions by using a high pressure vessel. The reaction conditions are optimized by studying the effects of reaction parameters on the yield of products. The maximum total yield of two kinds of small molecule organic acids (lactic acid and formic acid) and HMF is 51.94%.

II. EXPERIMENTS

A. Materials

Graphite powder, $KMnO_4$, $NaNO_3$, $98\%H_2SO_4$, $30\%H_2O_2$, 12 mol/L HCl, tetrahydrofuran (THF), and glucose ($C_6H_{12}O_6 \cdot H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd., and were used directly without further purification. Sodium hydride (80%NaH) and propane sultone were purchased from Aladdin Industrial Corporation and J&K Scientific Co., Ltd., respectively. Ultrapure water (18 MΩ) was produced by a Millipore System (Millipore Q, USA).

B. Synthesis of GO and rGO-SO₃H

Graphite oxide (GO) was prepared from natural graphite by the well-known modified Hummers method. $rGO-SO_3H$ was synthesized by using NaH and propane sultone. Here, NaH was used to react with -OH groups of GO nanosheets and propane sultone was used as sulfonated reagent to provide $-SO_3H$ therein [16]. As a typical run, 0.2 g of the as-prepared GO were added into 100 mL of anhydrous THF and was dispersed under the assistance of ultrasound for 2 h, and 1.5 g NaH dispersed in 20 mL of THF were added slowly to the above GO/THF mixture, next the as-prepared mixture was heated at 60 °C under stirring for 6 h. Next, 2.5 g of propane sultone was added dropwisely into the as-prepared product, and the mixture was then reacted at 80 °C for 24 h under stirring. Then the isolated solid product was immersed into a 1 mol/L HCl solution under stirring for 12 h, after that, the suspension was centrifuged by washing several times with ethanol and ultrapure water. Finally, $rGO-SO_3H$ powder was obtained by freezing and drying of the suspension for 24 h.

C. Characterization

Fourier transform infrared (FT-IR) spectra of the samples were analyzed by a FT-IR spectrometer (Tensor27, Bruker, Germany). Thermogravimetric analyzer (Q5000IR, TA, USA) was used to measure the thermal stability of as-prepared samples, and all of the measurements were carried out under nitrogen gas over a temperature range of 25−800 °C with a ramp rate
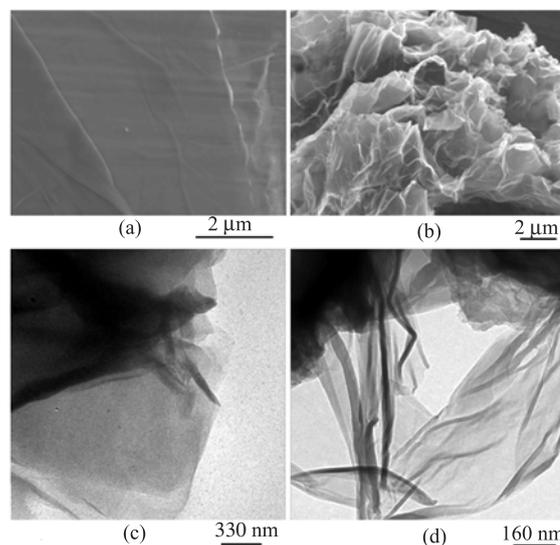

FIG. 1 SEM images of (a) GO and (b) $rGO-SO_3H$, TEM images of (c) GO and (d) $rGO-SO_3H$.

of 10 °C/min. Element analyzer (Vario EL III, Elementar, Germany) was used to analyze the element (C, H, N, and S) content. X-ray photoelectron spectroscopy (XPS) of samples was characterized by an Escalab250 photoelectron spectrometer (Thermo-VG Scientific Ltd., USA). The surface topography of samples was recorded by a scanning electron microscope (SEM, Sirion200, FEI, the Netherlands). TEM images of samples were taken by a high resolution transmission electron microscope (TEM, JEOL-2010, Japan). The reaction products were analyzed by using a high performance liquid chromatography (HPLC, LC-20AD, Shimadzu Corporation).

III. RESULTS AND DISCUSSION

SEM and TEM are very effective methods to study the surface topography and microstructure of as-obtained samples. Figure 1 (a) and (c) show the typical SEM and TEM images of GO powder, while Fig.1 (b) and (d) display SEM and TEM images of $rGO-SO_3H$, respectively. From the SEM images, it can be clearly found that $rGO-SO_3H$ shows a much stronger degree of folding than that of pure GO. In addition, compared with GO nanosheet, the $rGO-SO_3H$ nanosheet presents a state of fluffy and looks like a flower, which prevents the aggregation of the nanosheets and favors the catalytic reaction. At the same time, the TEM images of GO and $rGO-SO_3H$ show clearly similar feature of surface, and all of them are in a single layer.

FT-IR was used to prove the existence of the sulfonic acid groups which provided H^+ to catalytically degrade glucose to more valuable organic acids. As shown in Fig.2, the spectrum of GO mainly includes four kinds of characteristic peaks: carbonyl C=O (1727 cm^{-1}), aro-
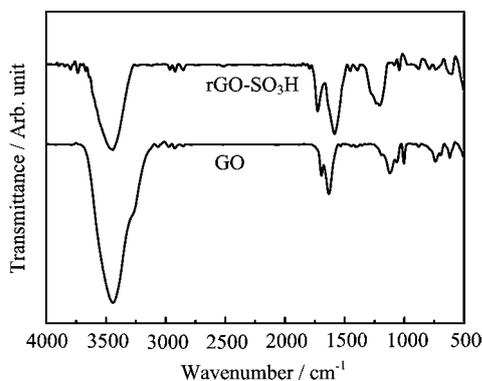
FIG. 2 FT-IR spectra of GO and rGO-SO$_3$H.
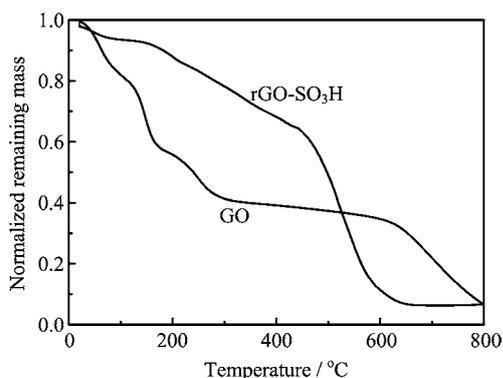
FIG. 3 TGA curves of GO and rGO-SO$_3$H.

matic C=C (1633 cm^{-1}), hydroxyl O−H (3466 cm^{-1}), C−O (1124 cm^{-1}). However, peaks at 1210 and 1043 cm^{-1} observed in the spectrum of the sample rGO-SO$_3$H are associated with the S=O bond in the sulfonic acid groups. It is obvious that the sulfonic acid groups were grafted successfully to the partially reduced GO [17].

To further prove the existence of the sulfonic acid groups in the rGO-SO$_3$H, elemental analysis was used to measure the content of C, H, and S. The results of content of elements of as-prepared samples are listed in Table I. Obviously, after reduction reaction with NaH, the content of sulfur in rGO is only 1.32%, may confirm that there are some sulfide residues. For rGO-SO$_3$H, the content of S is 5.53, indicating the successful grafting of sulfonic acid groups onto the surface of rGO. Meanwhile, the rGO-SO$_3$H has a C/H ratio of 21, which is similar to that of rGO reduced by NaH, much higher than that of GO. These results indicate that GO has been reduced partially.

The comparison of the thermal stability for the GO and rGO-SO$_3$H can be judged by the TGA measurement. Figure 3 shows the TGA curves of the GO and rGO-SO$_3$H. GO displays a weight loss at around 100 °C, which can be explained by the removal of absorbed water. The loss of mass at around 200 °C can be
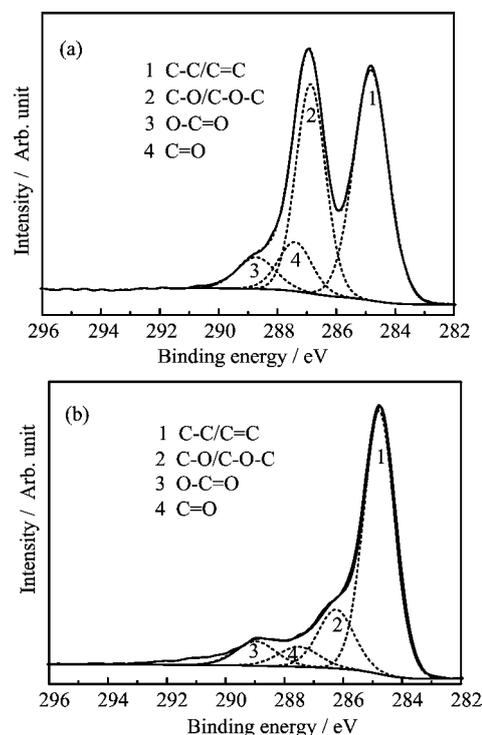
FIG. 4 XPS survey spectra of (a) GO and (b) rGO-SO$_3$H.

TABLE I Elemental analysis results of GO, rGO (reduced by NaH) and rGO-SO$_3$H.

Sample	C/%	H/%	S/%
GO	39.30	3.22	4.52
rGO	57.80	2.79	1.32
rGO-SO$_3$H	60.06	2.86	5.53

ascribed to the removal of oxygen-containing functional groups. On the other hand, there is little weight loss at around 200 °C in the TGA curve of rGO-SO$_3$H, indicating that the GO has been reduced partially, which is in good agreement with the result of elemental analysis. At the same time, the TGA curve of rGO-SO$_3$H exhibits a loss of mass at around 258 °C, and the loss of weight at around 500 °C can be attributed to the decomposition of the sample framework, these results indicate that the thermal stability of the rGO-SO$_3$H is much better than that of GO, which is beneficial to the recycling of the catalyst [18].

XPS is a powerful technique to confirm the states of surface elements of as-obtained samples. Figure 4 shows the typical C1s spectra of GO and rGO-SO$_3$H respectively, it is clearly seen that the C1s spectra of the GO consists of four main characteristic peaks: C=C/C−C (non-oxygenate ring carbon, 284.82 eV), C−O/C−O−C (the carbon in the C−O bond, 286.87 eV), C=O (carbonyl, 287.4 eV), O=C−O (carboxyl, 288.72 eV). However, after sulfonation of

TABLE II The yield of organic acids, including formic acid (FA) and lactic acid (LA), and HMF for the reaction of hydrolysis of glucose at different content of catalyst.

Glucose/mg	rGO-SO$_3$H/mg	Gluose/rGO-SO$_3$H	FA/%	LA/%	HMF/%	Total yield/%
83	5	16.6	10.97	6.38	20.25	37.6
84	7	12.0	11.40	5.82	20.48	37.7
85	10	8.5	13.05	5.51	21.21	39.77
83	13	6.4	10.72	4.61	14.5	29.83

Note: reaction conditions were temperature at 180 °C, time of 3 h, and 20 mL of H$_2$O.

the pure GO, the intensity of oxygen-containing functional groups peaks decrease sharply, suggesting that the oxygen-containing groups have been partially removed [18].

In order to study the catalytic activity of the as-obtained sulfonated graphene, the reaction of degradation of glucose was used, which was regarded as the standard reaction. In our study, the reaction of degradation of glucose was carried out in a high pressure vessel (50 mL, Parr Instrument Company, USA), and it is equipped with a magnetic stirrer and a program temperature controller. After reaction, the reaction solution was filtered and a yellow solution was obtained, then the solution was diluted with ultrapure water to 100 mL. Next, the as-prepared product was filtered by the syringe membrane filter, which included small molecule organic acids and HMF, and then it can be directly analyzed by using HPLC equipped with an UV-Vis detector (SPD-20A, Japan).

At first, the influence of catalyst dosage on the hydrolysis of glucose was studied to get the best ratio of glucose/rGO-SO$_3$H. The reaction is performed at different ratios from 16.6 to 6.4. As shown in Table II, the product contains two main small molecular organic acids and HMF. The HMF is the major product with a yield of 20.25%, and the yields of formic acid and lactic acid are 10.97% and 6.38% respectively when the ratio of glucose/rGO-SO$_3$H is 16.6. Meanwhile, the total yield of three products is 37.6%. It is clear to see that the optimal catalyst dosage is about 8.5, which shows a maximum yield of 39.77%. However, the total yield of acids decreased from 39.77% to 29.83% when the ratio of glucose/rGO-SO$_3$H decreased from 8.5 to 6.4, indicating that an excess of catalyst dosage is unfavorable for the glucose conversion. The most probable reason is that the glucose cannot easily access the active sites of the catalyst.

Additionally, the effect of reaction temperature on the glucose conversion was also explored. The reactions were carried out at 160, 180, 200, and 220 °C, respectively. Table III shows the yields of different product obtained at different temperature, and it can be found that the reaction temperature has a great impact on the yield of products and the yield of HMF increase sharply from 5.25% to 24.02% when the temperature was increased from 160 °C to 200 °C. Clearly, at 200 °C,

TABLE III The yield of organic acids and HMF for the reaction of hydrolysis of glucose at different temperature.

T/°C	FA/%	LA/%	HMF/%	Total yield/%
160	9.64	4.15	5.25	19.04
180	13.05	5.51	21.21	39.77
200	14.18	7.45	24.02	45.65
220	12.34	3.97	10.06	26.37

Note: reaction conditions were 0.08 g of glucose, 0.01 g of rGO-SO$_3$H, 20 mL of H$_2$O, and time of 3 h.

TABLE IV The yield of organic acids and HMF for the reaction of hydrolysis of glucose at different reaction time.

t/h	FA/%	LA/%	HMF/%	Total yield/%
1	11.90	6.90	25.43	44.23
2	15.39	7.75	28.80	51.94
3	15.18	8.6	23.31	47.09
4	10.30	5.77	16.87	32.94

Note: reaction conditions were 0.08 g of glucose, 0.01 g of rGO-SO$_3$H, 20 mL of H$_2$O, temperature at 200 °C.

yield of formic acid reaches 14.18% with 7.45% of lactic acid, and the total yield of three kinds of products is 45.65%. However, the yield of HMF is 10.06% and the total yield of products is 26.37% when the temperature rose to 220 °C, these results indicate that side reaction may occur at higher temperature and the three main products is unstable at the same time. Therefore, the optimal reaction temperature to catalyze glucose conversion is considered as 200 °C.

The optimal reaction time is very important for the efficient conversion of glucose to the small molecular organic acids and HMF. As it can be observed from the Table IV, the reaction time has a little effect on the yield of acids. The reaction time of 2 h is found to be the most suitable condition, which gives the highest total yields of 51.94%. Interestingly, the total yield of three products decrease to 32.94% when the experiment was carried out for 4 h, and the result reveals that the unwanted side product may appear. All in all, the most suitable reaction conditions are obtained: 0.08 g of glucose, 0.01 g of rGO-SO$_3$H, 200 °C, 2 h, 20 mL of H$_2$O.

TABLE V The recycling of the catalyst for the reaction of hydrolysis of glucose.

Run	FA/%	LA/%	HMF/%	Total yield/%
1	15.39	7.75	28.80	51.94
2	15.33	7.72	28.68	51.73
3	14.43	7.27	27.00	48.70
4	10.98	5.53	20.54	37.05
5	10.87	5.47	20.34	36.68

Note: reaction conditions were 0.08 g of glucose, 0.01 g of rGO-SO$_3$H, 20 mL of H$_2$O, temperature at 200 °C, and time of 2 h.

At the end, stability of rGO-SO$_3$H as a solid acid catalyst was investigated by the recycling experiment for five times. The yield of three main products and the total yield are summarized in Table V. It is observed that the total yield shows small changes for the first three times of recycling reaction. In addition, after five run experiments, the catalyst activity decreases slightly and the total yield of organic acids decreases from 51.94% to 36.68%. The above results of recycling experiment prove that the rGO-SO$_3$H exhibits relatively good stability for the hydrolysis of glucose.

IV. CONCLUSION

Here, a new sulfonated graphene catalyst was synthesized for conversion of glucose to valuable product, such as formic acid, lactic acid and HMF. The reaction condition is very important for the yields of products and we study the effect of various reaction conditions, including a catalyst dosage, temperature and reaction time. The highest yields of three kinds of product is found to be 51.94% when the experiment was performed at the optimal reaction condition (glucose 0.08 g, rGO-SO$_3$H 0.01 g, 200 °C, 2 h, H$_2$O 20 mL). In addition, compared to other liquid catalysts, the sulfonated graphene has many advantages, which mainly reflect in three aspects: environmentally friendly, recoverability, and low cost. The solid acid catalyst can be recycled five times with little decreases in activity, indicating that it shows relatively higher stability. Introducing more sulfonic acid groups to the surface of graphene is the key fac-

tor to affect the catalytic activity; future research will study this aspect and the industrialization application of the as-obtained catalyst.

V. ACKNOWLEDGMENTS

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