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Short communication

Graphene oxide as a facile solid acid catalyst for the production of bioadditives from glycerol esterification

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ABSTRACT

Graphene oxide (GO) has proved to be a highly active and reusable solid acid catalyst for glycerol esterification with acetic acid in the synthesis of bioadditives diacylglycerol (DAG) and triacylglycerol (TAG). The effects of reaction temperature, molar ratio of acetic acid to glycerol, catalyst amount and reaction time were investigated. A 90.2% combined selectivity of DAG and TAG with complete glycerol conversion was achieved at 120 °C for 6 h over GO. Final characterization shows that the active site of GO is the remaining SO_3H group.

1. Introduction

The limitation of fossil resources and global concerns regarding environmental issues stimulate the increasing attention for sustainable production of fuels from renewable biomass. Among them, biodiesel has attracted great interest because it possesses nontoxic, biocompatible as well as biodegradable features, and substantially reduces CO_2 emission. With the rapid development of biodiesel industry, abundant byproduct glycerol has been produced via the transesterification of vegetable oil with low alcohol [1]. Therefore, it is urgent to convert glycerol into valuable chemicals or biofuels to promote the benign development of biodiesel industry. Several innovative strategies have been designed to utilize glycerol involving hydrogenolysis [2], oxidation [3], esterification [4–6], etherification [7], polymerization [1] and so on. In this context, one of the most desirable processes is to perform glycerol esterification with acetic acid to produce monoacylglycerol (MAG), diacylglycerol (DAG) and triacylglycerol (TAG). These products are widely utilized in cryogenics, biodegradable polyester and cosmetics. Compared with MAG, DAG and TAG own much higher economic value because of their potential applications as valuable liquid fuel additives in improving octane number, cold and viscosity properties [8].

Significant acid catalysts have been used for glycerol esterification, including sulfated based superacids [9–11], heteropolyacid-based catalysts [12–14], Amberlyst-15 [15–18], tin chloride [19], zeolite [18], Y/SBA-3 [20], and ZrO_2 based solid acids [21]. Regardless of their great advances, most have the drawbacks of rapid deactivation, complex preparation procedures, low reactivity, and expensive costs. To overcome these disadvantages, it is imperative to develop a highly active, inexpensive, robust and sustainable solid acid catalyst for glycerol esterification.

Recently, graphene and graphene oxide (GO) have gained considerable interest due to their unique physical, chemical and electrical properties [22]. Prepared by Hummer's method, GO undergoes exhaustive oxidation and thus possesses rich oxygen-containing functionalities, such as SO_3H, carboxyl, hydroxyl and epoxide groups, which endows it with moderate acidic and oxidizing properties [23]. GO has been employed as an efficient carbocatalyst in hydration [23], oxidation [23], Aza-Michael addition [24] and Friedel–Crafts addition [25]. Recently, GO has demonstrated to be a highly active and reusable solid acid carbocatalyst for furfuryl alcohol alcoholysis in our previous work [22]. Consequently, it is envisaged that GO may be a potential and facile solid acid catalyst for glycerol esterification with acetic acid. For the first time, GO is reported as an acid catalyst for glycerol esterification. Our results indeed show that GO is capable of achieving complete glycerol conversion with ~90% combined selectivity to preferred DAG and TAG. The unprecedented catalytic performance is related to the oxygen-containing groups, particularly the SO_3H groups.

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2. Experimental

2.1. Catalyst preparation

GO was prepared by a modification to the Hummer's method described elsewhere [22]. Briefly, graphite (5 g) and $NaNO_3$ (2.5 g) were introduced into 115 mL H_2SO_4 in an ice bath under vigorous stirring. The reaction system was heated to 35 °C and stirred for an additional 30 min after adding 15 g $KMnO_4$. This system was diluted by adding 230 mL deionized water, heated to 98 °C, and followed by adding 700 mL water. The mixture was filtered, washed and dried at 50 °C after introducing 50 mL H_2O_2 (30 wt.%). The dispersed graphite oxide in water was kept in sonication for 60 min, centrifugated and dried at ambient temperature.

The preparation methods of other catalysts (ZSM-48, ZSM-5, H-mordenite, WO_3/ZrO_2, MoO_3/ZrO_2, HPW/ZrO_2, and $Cs_{2.5}PW$) were depicted in supporting information.

2.2. Catalyst characterization

Scanning Electron Microscopy (SEM) was conducted on a JSM 7001-F microscope. EDX spectra were carried out using 20 kV primary electron voltages. The IR spectra were measured by Vertex 70 (Bruker) FT-IR spectrophotometer in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. The samples were mixed with KBr and pressed into translucent disks at room temperature. The S content was measured by elemental microanalysis (EA) (vario MICRO cube, Elemental).

2.3. Catalytic reaction

The catalytic tests for glycerol esterification with acetic acid were carried out in a stainless steel autoclave with a magnetic stirring. Typically, 2.0 g glycerol and 13.0 g acetic acid with 0.1 g GO were added into the reactor and then the mixture was heated to the desired temperature for a specified time. Reaction conditions were changed to investigate the dependence of main variables such as time, reaction temperature, catalyst loading and molar ratio of acetic acid/glycerol. When the reaction was terminated, the reactor was cooled in an ice-water bath. After the mixture was separated by centrifugation, the obtained products were diluted with ethanol and analyzed by GC with a FID using a DB-1 capillary column. Corrected area normalization method was used to quantify the products. The assignments of these products were also determined by GC–MS. The conversion of glycerol and selectivity of products were determined by using the following equations.

$$\text{Conversation}\,(\%) = \frac{\text{moles of glycerol (in)} - \text{moles of glycerol (out)}}{\text{moles of all glycerol (in)}} \times 100$$

$$\text{Selectivity}\,(\%) = \frac{\text{moles of one product}}{\text{moles of all product}} \times 100$$

3. Results and discussion

3.1. Catalyst characterization

The synthesized GO was characterized by SEM–EDX and FTIR. As indicated by SEM in Fig. 1, GO presented a crumpled and layered structure. EDX spectroscopy showed that GO primarily contained carbon and oxygen, as well as small amounts of sulfur. The large amount of oxygen was an indication of rich oxygen-bearing functionalities. The remaining sulfur confirmed the presence of SO_3H group, which can be further corroborated by FTIR (at around 1160 cm^{-1}) [26]. The EA results also showed that the S amount was as high as 1.21 wt.%, corresponding to 0.378 mmol/g SO_3H groups in GO. As displayed in Fig. 2, an intense and broad peak located at ca. 3400 cm^{-1}, corresponding to the stretching mode of OH bond. Additional hydroxyl peaks were located at 1390 cm^{-1} and 1085 cm^{-1}. The strong bands centered at 1640 cm^{-1} and 1730 cm^{-1} (νC=O) were ascribed to carboxylic acid and carbonyl groups. Additionally, the bands at 1260 cm^{-1} and 800 cm^{-1} reflected the appearance of C–O–C (epoxy) groups [22].

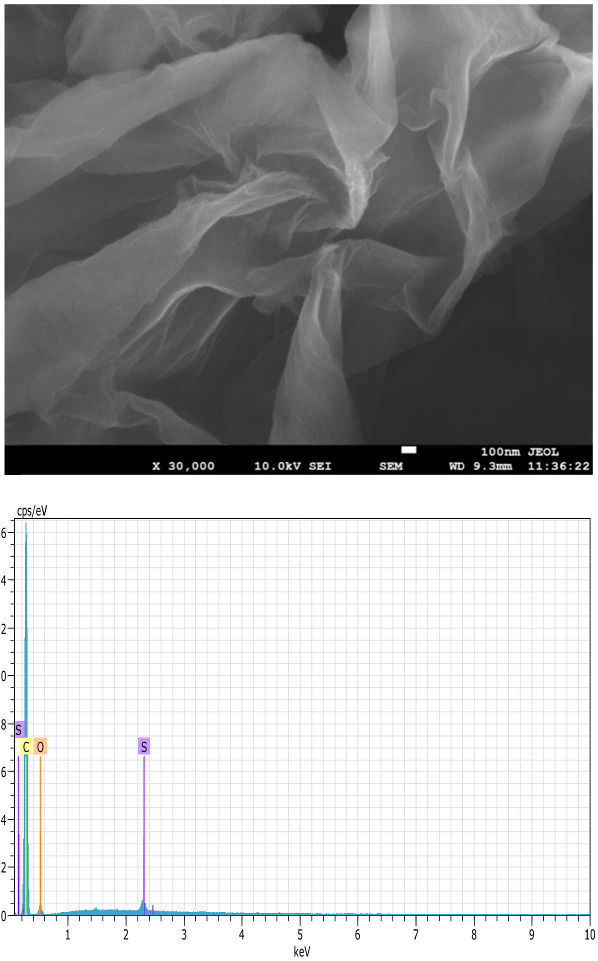

Fig. 1. Typical SEM–EDS image of GO.

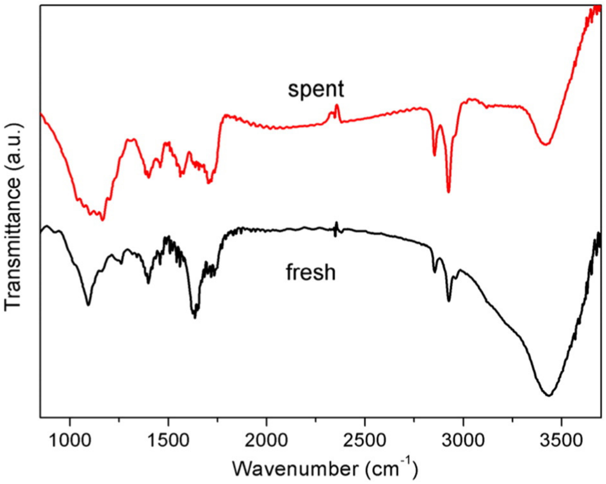

Fig. 2. FTIR spectra of fresh and spent GO.

Table 1
Catalytic performance of glycerol esterification with acetic acid over different catalysts.[a]

Catalyst	Conversion (%)	Selectivity (%)		
		MAG	DAG	TAG
Blank	48.9	31.8	63.3	4.9
GO	98.5	15.5	60.0	24.5
ZSM-48	68.0	35.7	58.0	6.3
ZSM-5	76.3	30.8	62.2	7.0
H-mordenite	75.0	35.3	58.3	6.4
WO_3/ZrO_2	74.2	36.9	56.7	6.4
MoO_3/ZrO_2	72.7	33.2	59.4	7.4
HPW/ZrO_2	73.2	38.7	55.4	5.9
$Cs_{2.5}PW$	73.0	34.9	59.2	5.9

[a] Reaction conditions: reaction temperature = 120 °C, molar ratio of glycerol with acetic acid = 1:10, catalyst amount = 0.1 g, reaction time = 1 h.

3.2. Catalytic esterification of glycerol

Table 1 displays the results from the reaction of glycerol esterification with acetic acid over GO and a series of representative solid acid catalysts. Even without the catalyst, 48.9% glycerol was converted to MAG, DAG and TAG, implying that glycerol esterification is a self-catalysis reaction wherein the acidic protons from acetic acid can catalyze this reaction itself. Compared to the blank experiment, ZSM-48 only presented minor promotion for this reaction due to lower acidity. Medium activities were obtained for strong acidic zeolites ZSM-5 and H-mordenite. Other catalysts, such as WO_3/ZrO_2, MoO_3/ZrO_2, HPW/ZrO_2 and $Cs_{2.5}PW$, showed ca. 70% conversion with low TAG selectivity. Surprisingly, excellent reaction performance was achieved for GO, 98.5% conversion and 24.5% TAG selectivity. The combined results clearly demonstrate the high efficiency of GO in glycerol esterification. GO contains 0.378 mmol/g SO_3H groups, which provides an abundance of acidic sites. As glycerol esterification is a typical acid-catalyzed reaction, the superior performance of GO should be mainly attributed to the large amounts of strong acidic SO_3H groups. Additionally, the unique layered structure facilitates to adsorb reactants and promote the reaction.

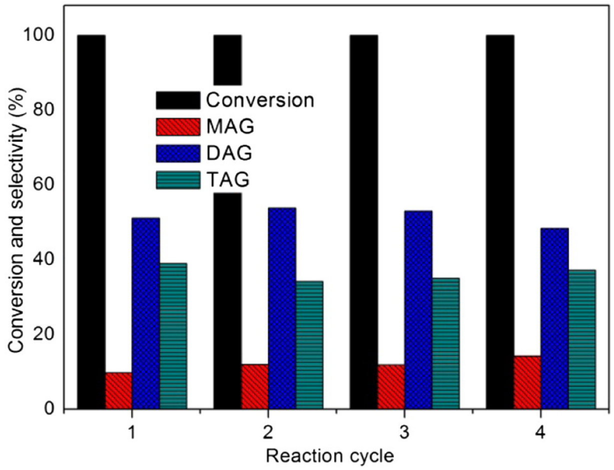

Fig. 4. Recycling results of glycerol esterification with acetic acid over GO catalysts. Reaction conditions: reaction temperature = 120 °C, molar ratio of glycerol with acetic acid = 1:10, catalyst amount = 0.1 g, reaction time = 6 h.

3.3. Influence of reaction conditions

Reaction temperature has significant impact on the catalytic activity and product distribution. As shown in Fig. 3A, glycerol conversion improved remarkably with the increasing reaction temperature and

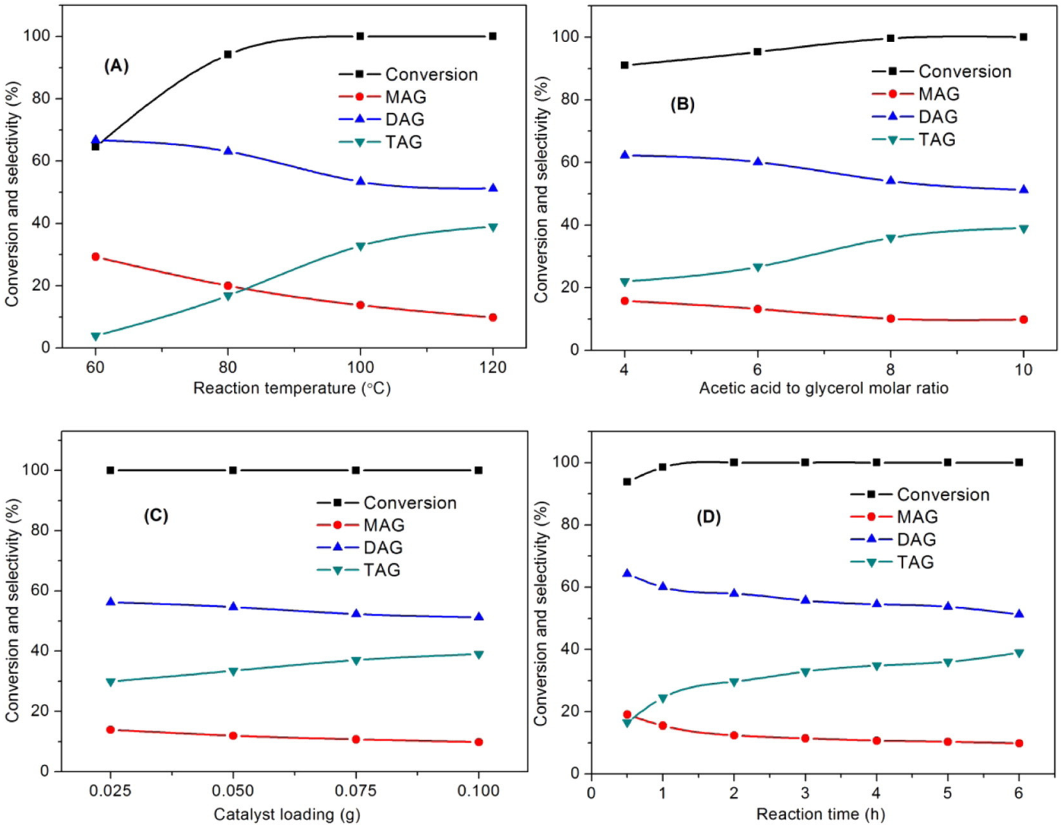

Fig. 3. Effect of reaction temperature (A), molar ratio of acetic acid to glycerol (B), catalyst loading (C) and reaction time (D) on the catalytic performance of glycerol esterification with acetic acid over GO catalysts. Reaction conditions: reaction temperature = 120 °C, molar ratio of glycerol with acetic acid = 1:10, catalyst amount = 0.1 g, reaction time = 6 h (except the variables).

reached 100% at 100 °C over GO catalyst. Simultaneously, the selectivity for TAG increased drastically with the increasing temperature at the expense of MAG and DAG, indicating that the improvement of temperature is instrumental in promoting the further esterification of MAG and DAG to produce TAG. Because glycerol consecutive esterification is a highly endothermic reaction, higher temperature facilitates to improve the extent of esterification [4].

Comparing the effect of temperature, molar ratio of acetic acid to glycerol had minor effect on glycerol conversion (Fig. 3B). GO presented good conversion, 91.0% at low molar ratio of 4:1. Nevertheless, the selectivity to TAG increased obviously with the increase in molar ratio of acetic acid to glycerol. The increase in acetic acid concentration provides more esterification agent which undergoes the formation of TAG through further esterification from MAG and TAG.

As illustrated in Fig. 3C, complete conversion of glycerol was achieved when using only 0.025 g GO, implying that GO is extremely active for glycerol esterification. Regarding the selectivity, the enhancement of catalyst loading slightly increased the selectivity to desired TAG.

The reaction time dependence of glycerol esterification over GO is illustrated in Fig. 3D. Glycerol conversion of 93.8% was obtained within just 30 min and reached 100% after 2 h. As the reaction proceeded, the selectivity to MAG and DAG declined while TAG selectivity increased correspondingly. These reactivity trends implicitly indicate the consecutive feature of glycerol esterification. The interaction of acetic acid with proton sites from GO results in the protonation of carbonyl group, which is attacked by glycerol and generated an acylium ion intermediate [6]. This intermediate tends to approach other acetic acid molecule and further proceeds consecutive nucleophilic attack on acetic acid. After reacting for 6 h, the combined selectivity of desired DAG and TAG was up to 90.2% over GO, which is among the best results (Table S1). Compared to the published reports, the combined yield to DAG and TAG is higher than that of $PrSO_3H$–SBA15 [9], sulfated zirconia [10], HPW/AC [13], Y/SBA-3 [20], and MoO_x/TiO_2–ZrO_2 [21].

3.4. Reusability test

As shown in Fig. 4, the recovered GO was reused four times without a decline in catalytic activity. Moreover, the product distribution did not show appreciable change during the complete test. The spent catalyst was characterized by FTIR; the results were compared with the fresh one in Fig. 2. As can be seen, the spent catalyst displayed similar structures with fresh GO, revealing that the oxygen-containing groups were mostly preserved during the reaction.

4. Conclusions

Compared to conventional solid acid catalyst, GO prepared by Hummer's method has demonstrated to be a highly active acid catalyst towards glycerol esterification to valuable bioadditives. The excellent performance of GO, complete glycerol conversion with 90.2% combined selectivity to DAG and TAG, was mainly attributed to the rich SO_3H groups and unique lamellar structure. Moreover, GO presented consistent conversion in consecutive catalytic tests. It can be envisioned that such a cheap and robust solid acid catalyst holds great potential for a wide range of acid-catalyzed reactions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2015.01.007.

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