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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].

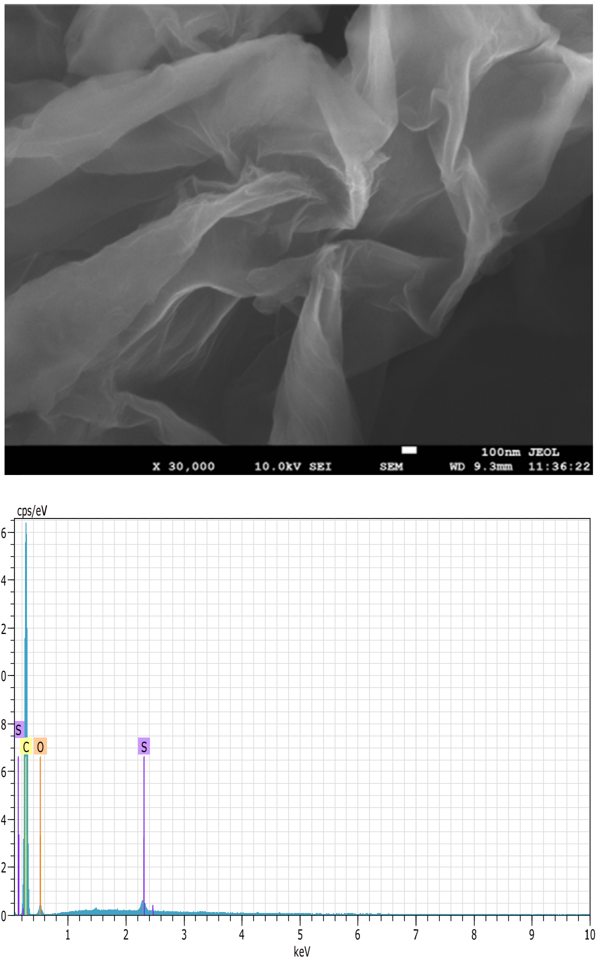

Fig. 1. Typical SEM–EDS image of GO.

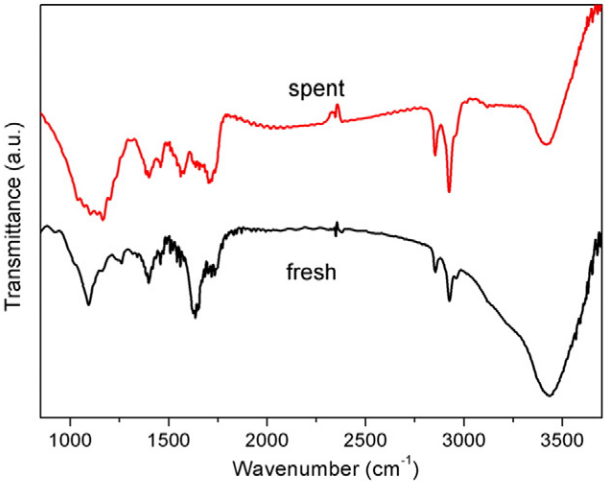

Fig. 2. FTIR spectra of fresh and spent GO.