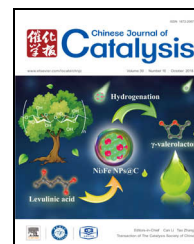


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Article

Modified graphene-based materials as effective catalysts for transesterification of rapeseed oil to biodiesel fuel



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ABSTRACT

Production of biodiesel by the transesterification process using different modified graphene-based materials as catalysts was studied. Solid acid graphene-based samples were prepared by grafting sulfonic or phosphate groups on the surface of thermally reduced graphene oxide. The obtained materials were thoroughly characterized using scanning electron microscopy, X-ray diffraction, thermogravimetric analysis, X-ray photoelectron spectroscopy, N₂ adsorption-desorption measurements, potentiometric titration, elemental analysis, and Fourier transform infrared spectroscopy. The prepared catalysts were tested in the transesterification of rapeseed oil with methanol at 130 °C under pressure, and their activities were compared to the performance of a commercially available heterogeneous acidic catalyst, Amberlyst-15. All modified samples were active in the transesterification process; however, significant differences were observed in the yield of biodiesel, depending on the method of catalyst preparation and strength of the acidic sites. The highest yield of fatty acid methyl esters of 70% was obtained for thermally reduced graphene oxide functionalized with 4-benzenediazonium sulfonate after 6 h of processing, and this result was much higher than that obtained for the commercial catalyst Amberlyst-15. The results of the reusability test were also promising.

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1. Introduction

Fossil fuels (petroleum, coal, and natural gas) are the main sources of energy in many parts of the world. However, the strong dependence on these non-renewable resources has raised serious concerns. First, experts have warned about the rapid depletion of fossil fuels, which is mainly related to the increasing world population, industrial and technological developments, and increasing demand for energy in developed and developing countries. Second, combustion of fossil fuels

generates many harmful products, e.g., carbon dioxide, nitrogen oxides, or particulate matter. Because of the aforementioned reasons, current research is focused on seeking fuels that are renewable and sustainable. The above approach also includes a gradual replacement of conventional diesel fuel by more environmentally friendly and biodegradable biodiesel [1,2].

Biodiesel is a mixture of fatty acid methyl esters (FAMES) and is usually produced through the transesterification of vegetable oils or animal fats with an alcohol in the presence of a catalyst [1]. Traditionally, strong Brønsted bases, such as so-

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dium or potassium hydroxide, or strong Brønsted acids, such as H_2SO_4 or H_3PO_4 , are used as homogenous catalysts for the transesterification reaction. However, the expensive separation of such catalysts from the reaction mixture has encouraged the development of heterogeneous systems for this process [3]. Solid catalytic systems have several advantages over homogeneous ones: they can be easily separated for reuse, they show less corrosive and toxic effects, and they are much more tolerant to water and free fatty acids (FFAs) in the feedstock [4]. For the last few years, there have been extensive studies on the performance of heterogeneous catalysts in transesterification reactions. Among the most commonly used systems are metal oxides or sulfides, zeolites, heteropoly acids, hydrotalcites, ion-exchange resins, basic oxides, and organic bases [4,5]. However, although the aforementioned materials are promising catalysts for biodiesel production, they still suffer from numerous drawbacks, e.g., easy deactivation, high cost, low thermal stability, and/or harmful effects on the environment because of the presence of certain metals [5]. In view of the above, current research is often focused on nanostructured carbon materials, which can be easily obtained using simple and economically viable methods, have tunable textural and chemical properties, and show a great catalytic potential [6–10].

Different carbon materials, including fullerenes, activated carbons, carbon nanotubes, and graphene, have been used in various processes as effective catalysts or catalyst supports [10–14]. Among them, graphene and its derivatives have attracted particular attention recently. Their usefulness in catalysis results from the following features: high theoretical specific surface area (up to $2630 \text{ m}^2/\text{g}$) and high chemical, thermal, optical, and electrochemical stabilities, which can potentially improve the lifetime of a catalyst. Moreover, the superior electron mobility of graphene facilitates electron transfer during the catalytic reactions, improving the catalytic activity [7,15,16]. Finally, chemically modified graphene, such as graphene oxide and reduced graphene oxide (also called “functionalized graphene sheets” [17]), can be obtained on a large scale at a relatively low cost using graphite as the starting material [18].

Literature concerning the use of graphene-based catalysts in the process of oil transesterification is very scarce. One of the most interesting papers regarding this topic was written by Nongbe et al. [19]. The authors reported that sulfonated graphene showed an excellent catalytic performance towards the transesterification of palm oil with methanol (yield of FAME, 98%). However, high methanol-to-oil molar ratio (20:1) and high catalyst loading (10 wt%) were used in this study. Although the methods of acid carbon catalyst preparation are relatively simple, it is still challenging to obtain materials with a high density of catalytic centers and to prevent these active sites against leaching from the carbon structure [10].

Taking the above into account, in the present study, we showed that thermally reduced graphene oxide (TRGO) modified with 4-benzenediazonium sulfonate (BDS), H_2SO_4 , or H_3PO_4 can be a promising solid acid catalyst to produce biodiesel from rapeseed oil, even when a relatively low molar ratio of methanol to oil and catalyst loading are used. The catalytic

activity and reusability of the samples were investigated and compared to the catalytic performance of a commercial catalyst, Amberlyst-15. The characterization of the graphene-based materials was performed, and the correlation between the structure of the catalysts and their performance in the transesterification reaction was discussed.

2. Experimental

2.1. Materials and reagents

The graphite used for the synthesis was of extra-pure grade. According to the manufacturer's data (Merck), its particle size was $\geq 50 \mu\text{m}$ ($\geq 99.5\%$). Commercially available rapeseed oil purchased in Poland was used in this work. All other reagents were of analytical grade or high purity and were used as received without further purification.

2.2. Preparation of catalysts

2.2.1. Synthesis of graphite oxide (GO) and TRGO

GO was synthesized from graphite according to the protocol reported by Yan et al. [20]. In a typical experiment, graphite powder was treated with concentrated H_2SO_4 , $\text{K}_2\text{S}_2\text{O}_8$, and P_2O_5 . The pre-oxidized sample obtained in this way was then subjected to oxidation by Hummers' method using NaNO_3 , H_2SO_4 , and KMnO_4 [21]. Afterwards, the prepared GO was washed thoroughly with distilled water until the pH of the filtrate was neutral. Finally, the obtained brown powder was dried in a desiccator to a constant weight. The simultaneous thermal exfoliation and reduction of GO was performed following the procedure described elsewhere [22]. Typically, the dried GO powder ($\sim 0.05 \text{ g}$) was quickly inserted into a vertical reactor that had been preheated by a tubular furnace (temperature of about $800 \text{ }^\circ\text{C}$). During this treatment, the argon flow rate through the reactor was maintained at $100 \text{ mL}/\text{min}$. The TRGO sample was then modified with different agents in order to introduce acidic functional groups on its surface.

2.2.2. Functionalization of TRGO with concentrated H_2SO_4

The treatment of TRGO with concentrated H_2SO_4 was performed as follows: TRGO (3.0 g) and concentrated H_2SO_4 (95 wt%, 140 mL) were placed in a three-neck round-bottom flask and heated at $140 \text{ }^\circ\text{C}$ for 5 or 20 h under an argon flow with continuous stirring. Then, the suspension was cooled to room temperature, and the obtained material was filtered and thoroughly washed with hot distilled water ($60 \text{ }^\circ\text{C}$). Finally, the sample was dried overnight at $110 \text{ }^\circ\text{C}$ and sieved to a uniform size range ($\leq 0.4 \text{ mm}$). The resultant catalysts are denoted as TRGO- H_2SO_4 -5 and TRGO- H_2SO_4 -20, where 5 and 20 represent the treatment time.

2.2.3. Functionalization of TRGO with BDS

Functionalization of TRGO with the diazonium cation generated *in situ* was performed according to a modified method proposed by Toupin et al. [23]. Briefly, TRGO (2.0 g) was dispersed in distilled water (100 mL); then, an equimolar amount

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