

## Catalytic performances of traditional $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Graphene Oxide and Graphene oxide-alumina in transesterification of oil to biodiesel

**Basant G. Salib, Hany M. Abdel Dayem and Fouad I. El-Hosiny**

Chemistry Department, Faculty of Science, Ain Shams University,  
11566 Abassia, Cairo, Egypt

### ABSTRACT

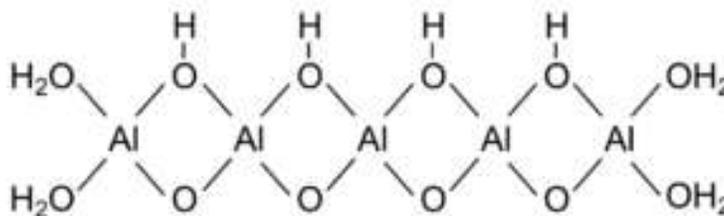
The catalytic properties of alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), Graphene Oxide (GO) and Graphene Oxide –alumina was studied in transesterification of sunflower oil to biodiesel. The catalytic tests were carried out at standard reaction conditions; reaction temperature 60°C, methanol to oil ratio 12:1, catalyst to oil ratio 1:100 and reaction time 1 hr. In the case of graphene oxide samples their performances in conversion of oil to biodiesel depends on the method of preparation. On the other hand, the catalytic activity results showed that addition of graphene oxide to alumina significantly improved its transesterification reaction where, conversion increased from 13% for neat alumina and 18% for GO to 28% for GO-alumina. This effect was attributed to that GO-alumina had higher amounts of acidic sites than its parent materials.

**Key words:** Catalytic performance,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Graphene Oxide, Graphene oxide-alumina, transesterification, sunflower oil , biodiesel.

### INTRODUCTION

Among the various transition alumina as  $\gamma$ -alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) is the most important catalyst and catalyst support in the automotive and petroleum industries. Its desired textural properties, such as surface area, pore volume, and pore-size distribution, and its acid/base characteristics are mainly owed to surface chemical composition, local microstructure, and phase composition<sup>[1]</sup>.

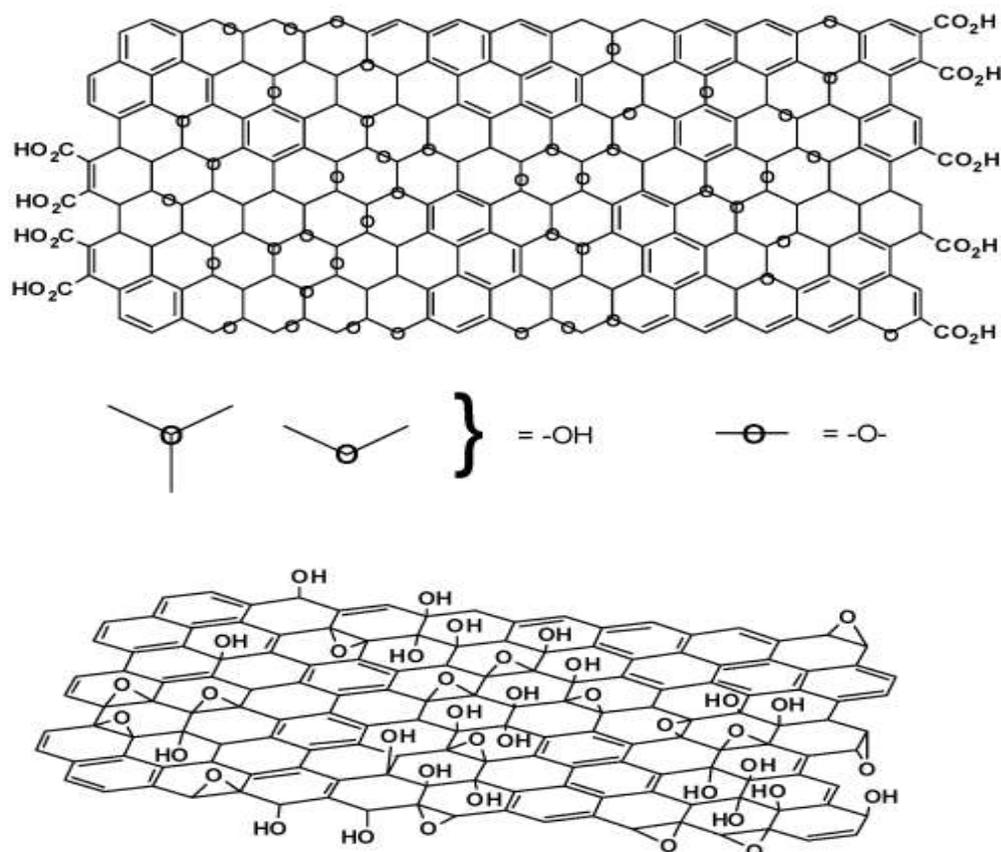
The catalytic properties (activity, selectivity, distribution of supported catalytic materials) of oxides (e.g., alumina) are intimately linked to their surface properties, because these chemical processes take place primarily on the surfaces of catalysts. Therefore, the chemical and physical characterization of Al<sub>2</sub>O<sub>3</sub> surfaces is crucially important for the correlation of catalytic properties with surface acidity (Fig. 1)<sup>[2]</sup>.



**Fig. 1. Acidic hydroxyl groups in alumina**

On the other hand, graphene oxide (GO) is a unique material that can be viewed as a single monomolecular layer of graphite. It is a compound of carbon, oxygen, and hydrogen in

variable ratios, obtained by treating graphite with strong oxidizers. The most recent models of GO have rejected the lattice-based model and have focused on a nonstoichiometric, amorphous alternative. Certainly, the most well-known model is the one by Lerf and Klinowski (Fig. 2). They have published several papers on the structure and hydration behavior of GO, and these are the most widely cited in the contemporary literature.



**Fig. 2. Variations of the Lerf-Klinowski model indicating ambiguity regarding the presence of carboxylic acids on the periphery of the basal plane of the graphitic platelets of GO<sup>[3]</sup>.**

As shown in Figure (2) GO structure includes several acidic oxygen-containing functionalities such as epoxide, carbonyl, carboxyl, and hydroxyl groups.

Use of biodiesel is growing quickly because of its excellent fuel properties. As fossil fuel reserves rapidly decline, renewable alternative fuels are more and more attractive. Diesel engines can be directly fueled with biodiesel without any mechanical change. Because biodiesel is renewable, biodegradable, and environmentally benign, engines fueled with biodiesel reduce the emission of toxic gases, such as  $\text{SO}_2$ ,  $\text{CO}$ , and hydrocarbons. Biodiesel consists of mono-alkyl esters of long-chain fatty acid manufactured by transesterification of vegetable oil or animal fat with methanol or ethanol. The transesterification reaction in traditional production of biodiesel is catalyzed by acid/base catalyst<sup>[4]</sup>.

Acid catalyst ( $\text{H}_2\text{SO}_4$ ) and basic catalysts ( $\text{KOH}$  and  $\text{NaOH}$ ) are usually the most effective homogeneous catalysts in alcohol transesterification reaction. However, using

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homogeneous catalysts causes significant problems in biodiesel products and process (viz, saponification, corrosion etc.). Using heterogeneous acid catalysts is a challenge in production of biodiesel from oil transesterification by alcohol however, these catalysts still suffered from low reactivity.

In the present study, we try to investigate the performance of a new series of acidic catalysts in production of biodiesel from methanol transesterification reaction of sunflower oil thus we have been investigated the reactivity of  $\text{Al}_2\text{O}_3$ , GO and GO- $\text{Al}_2\text{O}_3$  in this reaction.

### MATERIALS AND METHODS

#### Experimental procedures

##### 1. Catalysts Preparation

###### 1.1 Preparation of graphene oxide (GO)

Graphene oxide were prepared using Hummers' method with additional  $\text{KMnO}_4$ , Improved method<sup>[5]</sup>, exfoliation with microwave<sup>[6]</sup>, and exfoliation with ultrasonic<sup>[7]</sup>.

###### 1.2 Preparation of $\gamma$ -Alumina

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was used as aluminum precursor,  $\text{NH}_4\text{OH}$  as precipitator, a small amount of PEG4000 was added in the experiment. In order to reduce growth rate of the nucleation, the experimental temperature should be controlled below  $10^\circ\text{C}$ , dropping speed was controlled at 3 ~ 5 ml/min, and the end point pH value was kept between 7 and 8. After the end of the addition, the preparation of the precursor solution was prepared by aging and centrifugation, and then washed with anhydrous ethanol. Finally, the resulting sample was placed in a rapid heating furnace, with a temperature of  $10^\circ\text{C}/\text{min}$  rise to  $600^\circ\text{C}$  for 2h<sup>[8]</sup>.

###### 1.3 Graphene oxide – Alumina composite

Graphene oxide was added into deionized water and sonicated for 2 h to form GO(2) aqueous dispersion with well-dispersed nano sheets, alumina was added to the above-prepared GO for a period with stirring (typical case: 8 h), to be formed gradually at the  $\text{Al}_2\text{O}_3/\text{GO}$  dispersion interface.

###### 1.4 Catalysts Characterization techniques

Measurements of acid-base properties of catalysts (GO,  $\text{Al}_2\text{O}_3$ , GO- $\text{Al}_2\text{O}_3$ ) were performed by Boehm titration method and Point of zero charge (P.Z.C) was measured by potentiometric titration as shown in Figure (5).<sup>[9]</sup>

The pH-dependent surface charge characteristics of the samples were determined from acid-base titrations. The continuous potentiometric titrations were performed under  $\text{CO}_2$ -free condition using 0.1M  $\text{KNO}_3$  as background electrolyte at  $25^\circ\text{C}$ . The experiments were carried out using a micro-burette with a combination pH electrode calibrated in standard buffer solution. The required mass of kaolinite sample (0.1g) was added to the reaction vessel together with 60 mL of 0.1M  $\text{KNO}_3$  solution. The suspension was soaked for 18 h. In the procedure represented as base back-titration, BBT, the initial pH was noted and the suspension was titrated to pH 3.5 with  $\text{HNO}_3$  (0.01N). From pH 3.5 the system was titrated in step up to 10.5 with  $\text{KOH}$  (0.01N) and then with acid down to pH = 4.

Addition of alkaline solution causes an increase in pH and hence in  $\Gamma_{O^-}$  as the result of the dissociation of weaker acid sites. Also, the  $\Gamma_{H^+}$  decreases and thus, the surface excess charge decreases and approaches zero. Calculation of surface charge was performed directly from the measured pH and acid or base added at each data point. The specific net proton surface charge density,  $\delta$  ( $\text{mol L}^{-1} \text{g}^{-1}$ ), whether in the form of  $M-O^-$  or  $M-OH_2^+$  can then be calculated at each titration point as

$$\delta = C_A - C_B - [H^+]_{\text{measured}} + [OH^-]_{\text{measured}}$$

Where  $C_A$  and  $C_B$  are the concentrations of acid and base added to the suspension, respectively, and  $(C_A - C_B)$  corresponds to TOTH (total proton concentration in the system,  $\text{mol L}^{-1}$ )

The solution pH at the zero charge ( $\delta = 0$ ), that is in presence of equal amounts of the negative and positive charges, is called the point of zero net proton charge (PZNPC). The solid catalyst can generally be considered acidic, amphoteric and basic in nature when PZNPC ranged from 0.4-2, 3.9-9 and 8.9-12.7, respectively. In acidic samples,  $\Gamma_{O^-}$  exceed  $\Gamma_{H^+}$  and the surface excess charge becomes negative ( $M-O^-$ ). By addition of alkaline, it reacted with the free  $H^+$  and  $\Gamma_{H^+}$  exceeds  $\Gamma_{O^-}$  and hence and the surface excess charge becomes positive ( $M-OH_2^+$ ). The number of silanols and aluminols can be estimated approximately from the titration curves were the specific net proton surface charge densities were plotted versus pH as mentioned later in acid-base studies for solid catalyst samples.

FTIR analysis was carried out by Fourier transform IR spectrophotometer (Perkin-Elmer 293 FTIR, Thermo Scientific, USA) in the range of 400-4000  $\text{cm}^{-1}$ . X-ray diffraction analysis (XRD) was performed using AnUltima + X-ray diffractometer (Rigaku, SmartLab) with Cu-K $\alpha$  radiation at  $\lambda = 1.5406 \text{ \AA}$  in the  $2\theta$  range from  $5^\circ$  to  $80^\circ$  with a step width of  $0.01^\circ$  at room temperature.

### 1.5 Catalytic activity measurements

The equipment includes a 1000 cc glass container with a hot plate and stirrer, a thermocouple, a thermocouple reader, and a water condenser. The maximum reaction temperature,  $60^\circ\text{C}$ , was selected because it is just slightly below the boiling point of methanol, so the reaction vessel does not need to be pressurized. During the reaction, any evaporated methanol will be returned to the glass container by the condenser. The mixture was stirred at the same rate for all runs. This system was used for investigating acid catalyzed pretreatment of high FFA level feedstocks. The reaction followed up using AOCS officialmethod CA 14-56 for total, free and combined glycerol test<sup>[10]</sup>.

## RESULT AND DISCUSSION

### FTIR and XRD of GO

The transformation of Graphite to graphene oxide was verified by both FTIR and XRD (Figs. 3 and 4). Where, the FTIR peak at  $960 \text{ cm}^{-1}$  confirmed the oxidation of graphite to graphene oxide. In addition, the XRD band at  $11.9^\circ$  confirmed the formation of graphene oxide phase in these samples.

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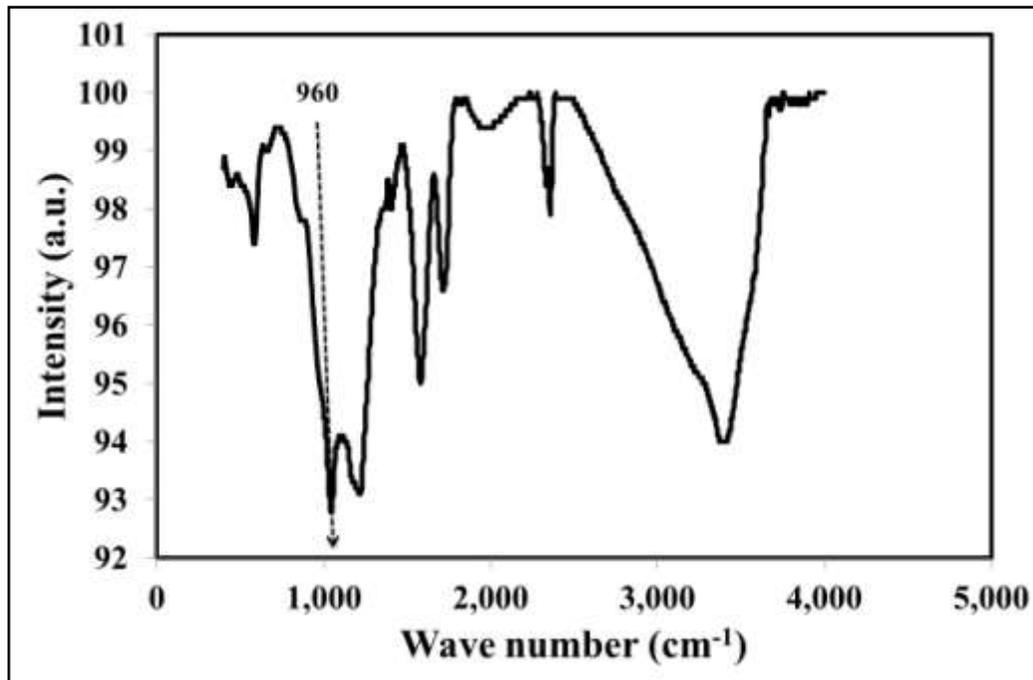


Fig. 3. FTIR of Graphene oxide

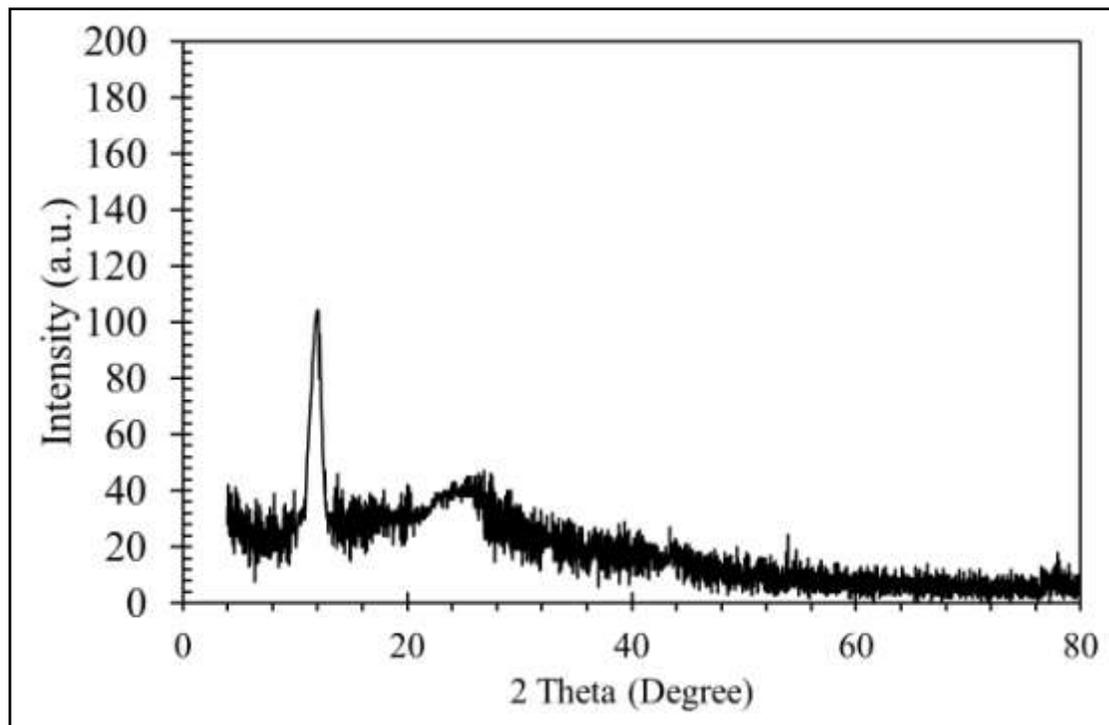


Fig. 4. XRD of Graphene oxide

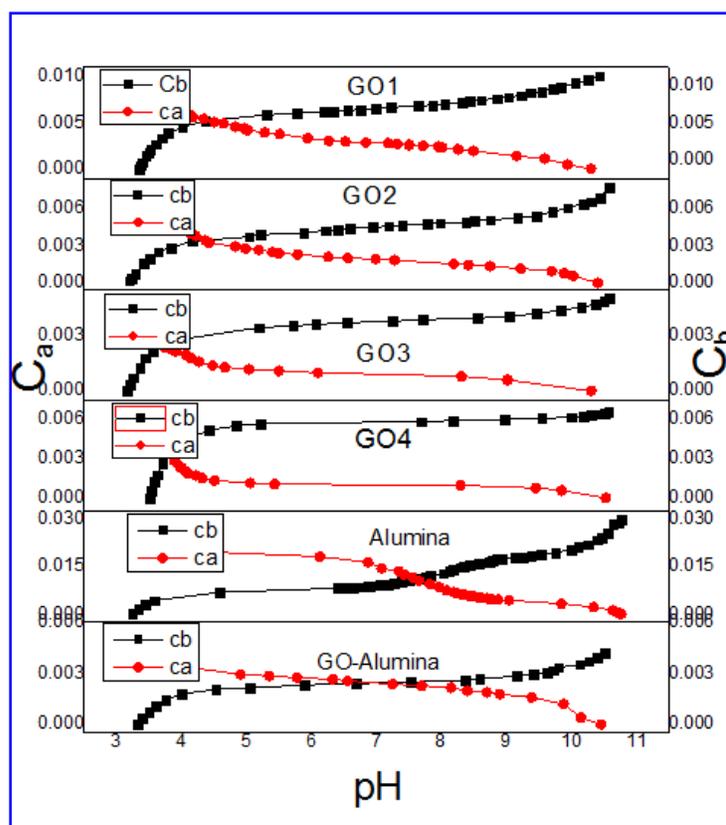
### Boehm method- oxygenous groups

The presence of oxygenous groups was quantified via Boehm titrations (Table 1). It is clear that, graphene oxide containing different oxygenous functional groups (viz., carboxylic, lactonic and acidic OH (phenolic)). In general, most of GO samples have the same functional groups. However, the amounts of these groups' dependent on the method of preparation. Where, the sample prepared by improved method exhibited the higher amount of acidity.

**Table 1.Boehm titration for GO samples, alumina and GO-alumina.**

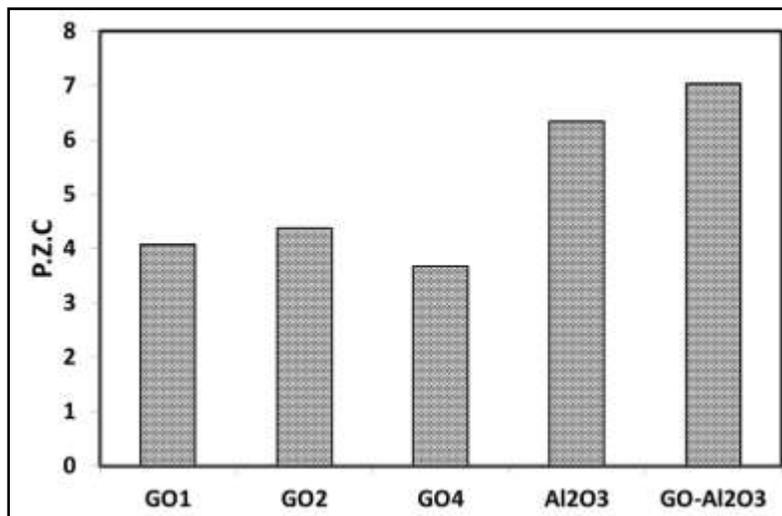
sample	carboxylic gps (mmol/g)	lactonicgps (mmol/g)	acidic OH gps (mmol/g)	Total acidity (mmol/g)
GO(1)	3.05	1.34	2.78	7.17
GO(2)	4.88	1.86	2.14	8.88
GO(3)	0.73	0.97	0.00	1.7
GO(4)	1.68	1.49	3.67	6.84
Al <sub>2</sub> O <sub>3</sub>	-	-	3.94	3.94
GO-Al <sub>2</sub> O <sub>3</sub>	4.15	0.00	5.20	9.35

### Point of zero charge



**Fig. 5. Acid base titration for different types of GO, alumina and GO-alumina. Where Ca concentration of acidic group and C<sub>b</sub> concentration of base.**

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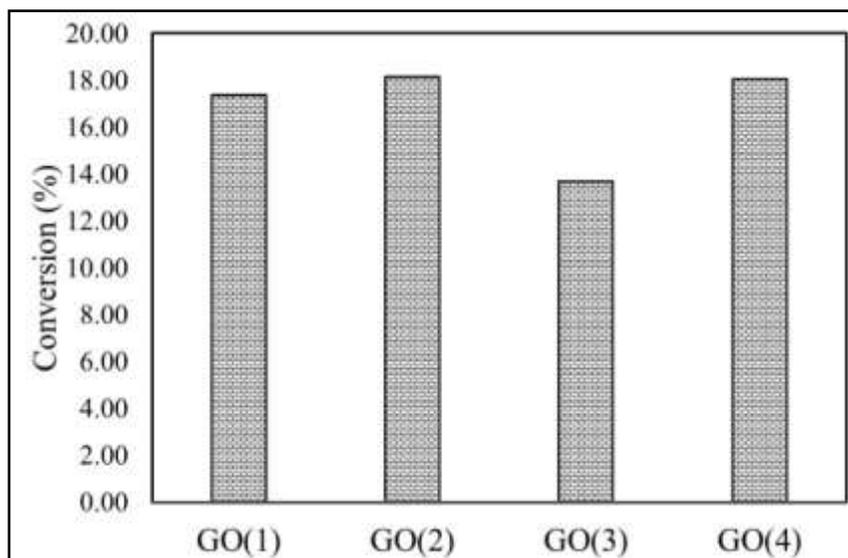
**Fig. 6.P.Z.C for GO, alumina and GO-alumina.**

As shown in Figure (6) the P.Z.C of neat Go samples or alumina was shifted to higher value when alumina modified by GO. Which indicating the presence of a strong interaction between GO and alumina this resulted in exposure of more oxygen groups on the surface as reflected by increase of total acidity of GO-alumina observed by Boehm titration.

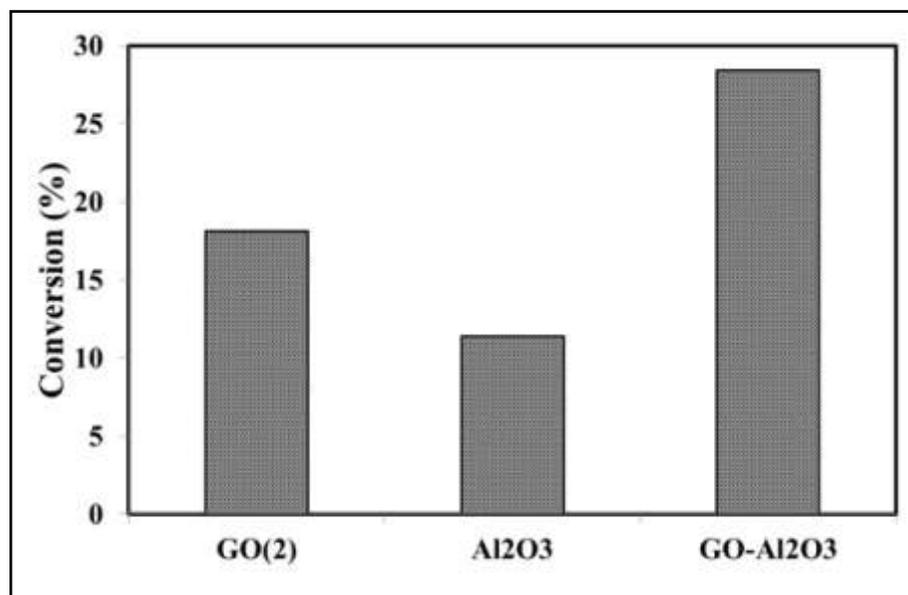
#### Catalytic activity

Figure (7) displays the catalytic performance of graphene oxide samples prepared by different methods in methanol transesterification of sunflower oil. It is clear that the sample (GO 2) prepared by improved method is the most active catalyst. According, Boehm titration results in Table (1) this can be attributed to that the GO1 has higher amount of total acidity ca. 8.8 mmol/g.

In addition, as shown in Figure (8) GO-Alumina composite achieved higher activity in methanol transesterification reaction of sunflower oil than either neat graphene oxide or neat alumina. Again, this higher activity of GO-Alumina can be ascribed to that it has higher amount of total acidity (Table 1). It seems that the assumed interaction between alumina and graphene (see; shift in P.Z.C) exposed more surface acidic active groups to the reactants.



**Fig. 7.** Catalytic activity of GO samples, in methanol transesterification of sunflower oil at 60°C, 1h and methanol to oil ratio 12:1.



**Fig. 8.** Effect of addition of GO to alumina in its catalytic performance

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### Conclusions

The activity of graphene oxide samples in methanol transesterification of sunflower oil depends on the amounts of acidic oxygen groups in the samples which in turn were changed by modifying method of preparation. A parallel significant enhancement was observed in the performance of either neat graphene oxide or neat alumina when they are transferred to composite namely, formation of 50wt% graphene oxide-50 wt% alumina composite. The higher performance of composite was attributed to the presence of higher exposed amount of acidic oxygen groups due the interaction between composite components. However, this catalyst is still need further improvement where conversion is not so high. These results recommend that GO-alumina composite can be used as a heterogenous catalyst or a support in conversion of oil to biodiesel.

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## الاداء التحفيزى لـ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> التقليدية وأكسيد الجرافين وأكسيد الجرافين والألومينا في تحويل الزيت إلى وقود الديزل الحيوي

بسنت صليب ، هاني عبد الدايم ، فؤاد الحوسيني

قسم الكيمياء ، كلية العلوم ، جامعة عين شمس ، 11566 العباسية ، القاهرة ، مصر

### المستخلص

تمت دراسة الخواص النحفزية لـ ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) وأكسيد الجرافين وأكسيد الجرافين والألومينا في عملية تحويل زيت عباد الشمس إلى وقود الديزل الحيوي. أجريت الاختبارات التحفيزية في ظروف التفاعل القياسية ؛ درجة حرارة التفاعل 60 درجة مئوية ، نسبة الميثانول إلى الزيت 12:1 ، نسبة المحفز إلى الزيت 1:100 وزمن التفاعل 1 ساعة. في حالة عينات أكسيد الجرافين يعتمد أدائها في تحويل الزيت إلى وقود الديزل الحيوي على طريقة التحضير. من ناحية أخرى ، أظهرت نتائج النشاط الحفزي أن إضافة أكسيد الجرافين إلى الألومينا قد حسن بشكل كبير من تفاعل تحويله حيث زاد التحويل من 13 ٪ للألومينا إلى 18 ٪ لأكسيد الجرافين و 28 ٪ لأكسيد الجرافين وللألومينا. ويعزى هذا التأثير إلى أكسيد الجرافين وللألومينا الذي يحتوي على كميات أعلى من المواقع الحمضية من المواد الأم.