

Synthesis of Graphene Oxide Sulfonated and Estimation of its Catalytic Activity in Conversion Reaction of Fructose to 5-Hydroxymethylfurfural

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Abstract: Graphene oxide (GO) was synthesized by Hummer method and sulfonated by $(\text{NH}_4)_2\text{SO}_4$ solution. The obtained material was characterized by different methods such as XRD, IR, TEM, EDS. The XRD pattern showed the successful exfoliation of graphite with shift of diffraction maximum from $2\theta=26,5^\circ$ to $10,4^\circ$. The TEM images released the existence of graphene oxide sheet in various sizes. The sulfo group formation ($-\text{SO}_3\text{H}$) on graphene oxide surface was confirmed by IR spectra with the appearance of characteristic picks at 1401 cm^{-1} và 1124 cm^{-1} attributed to vibrations of groups S-O and S=O. Catalytic activity of GO- SO_3H was estimated by reaction of fructose conversion into 5-hydroxymethylfufural (HMF). The different reaction parameters (temperature, time, solvent), were examined. It results that highest yield reaction attained 56% at 120°C , for 2h of reaction time and in solvent dimethyl sulfoxide (DMSO).

Keywords: 5-hydroxymethylfurfural, graphene oxide, fructose.

1. Introduction

With the rapid development of the industry, world-wide demand for fuels is increasing. Beside this, environmental requirement for fuels is more and more restricted. Bio-fuels seem to be met this demand. This fuel is renewable and don't emit CO_2 , one of the most greenhouse gas. The biofuels are formed mainly

from biomass, such as vegetable oils and lignocelluloses [1]. Between the two sources, fuel from lignocelluloses has more attention due its abundant lignocelluloses source and non-competitive with agricultural land. To synthesize biofuel from this source, one of the interesting ways passes an important intermediate compound, that is 5-hydroxymethylfurfural (HMF). HMF is synthesized from glucose or fructose through triple dehydration. Glucose and fructose can be obtained quite easily by hydrolysis of

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lignocelluloses. Dehydration of fructose (or glucose) reaction occurs in presence of acid homogeneous (NH_4Cl , H_2SO_4 ...) [2, 3] or acid heterogeneous catalyst ($\text{ZrO}_2\cdot\text{SO}_4$, Amberlyst-15 ...) [4, 5]. Between two types of catalyst, heterogeneous catalyst is more focused in recent studies by the advantage of separation product from reactive system. For this orientation, in this study, the acid heterogeneous catalyst, graphene oxide sulfonated, was synthesized and estimated for its catalytic activity through fructose conversion reaction of fructose to HMF.

2. Experimental

2.1. Catalyst preparation

All used chemicals have analytical purity: graphite (Sigma-Aldrich, 99%), H_2SO_4 (China, 98%), Fructose (Merk, 99%), KMnO_4 (China, 99%), $(\text{NH}_4)_2\text{SO}_4$.

The GO was prepared by modified Hummer method [6]. The sulfonation of GO was resumed as following: 1g of GO was added into 100ml distilled water and sonificated for 6h. After that, an adequate amount of $(\text{NH}_4)_2\text{SO}_4$ was diluted in this mixture and stirred at 50°C until obtain dried solid. This one calcined at 240°C under N_2 for 1h.

2.2. Catalytic characterisations

X-ray powder diffraction (XRD) measurements were carried out on D8 Advance Bruke apparatus with CuK_α radiation. TEM images were carried out on apparatus JEOL-JSM 5410LV.

IR spectrum of catalysts was measured on FTIR 8101M SHIMADZU. The EDX analysis was performed by Nova nanoSem 450 (FEI).

The products of fructose conversion were analysed by Shimadzu HPLC using a detector PDA and Cadenzal C18 column (250 mm x 4,6 mm, $3\ \mu\text{m}$) at 30°C . A mixture of acetonitrilne and water was used as the mobile phase with a flow rate of 1ml/min.

2.3. Catalytic activity test

For each catalytic test, 0,5g of fructose and 0,5g of $\text{GO-SO}_3\text{H}$ were added, mixed and stirred in 10ml of dimethylsulfoxide. The reaction was carried out under nitrogen atmosphere in an autoclave. HMF was quantified by HPLC.

3. Result and discussion

3.1. Characterisation of catalysts

X ray patterns of graphite and graphene oxides were presented in figure 1. The shift of the maximum diffraction at $2\theta = 26.5^\circ$ to 10.4° confirmed the success of exfoliation of graphite layer. The TEM images showed clearly layers of graphite and graphene oxide.

To determine the different functional groups on the graphene oxide surface, IR characterisation was performed (fig. 2a). From the characteristic of vibrations, It was noted that GO sulfonated ($\text{GO-SO}_3\text{H}$) sample contained different functional groups and bonds such as $-\text{OH}$ ($3126\ \text{cm}^{-1}$), $\text{C}=\text{O}$ in acid or carbonyl group ($1720\ \text{cm}^{-1}$), $\text{C}=\text{C}$ of the aromatic ring ($1401\ \text{cm}^{-1}$). Especially, the two absorption bands at $1401\ \text{cm}^{-1}$ and $1124\ \text{cm}^{-1}$ were attributed for vibration of covalent bonds S-O and S=O [7]. This one indicated the formation of $-\text{SO}_3\text{H}$ groups in GO structure.

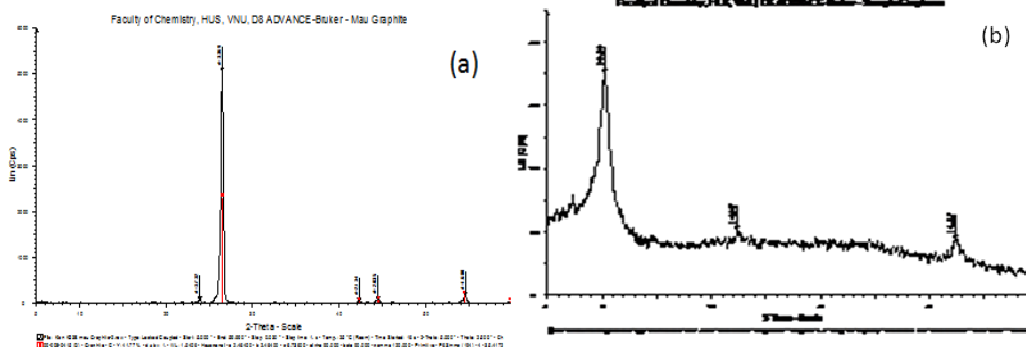


Figure 1. XRD patterns of graphite (a) and graphene oxide (b).

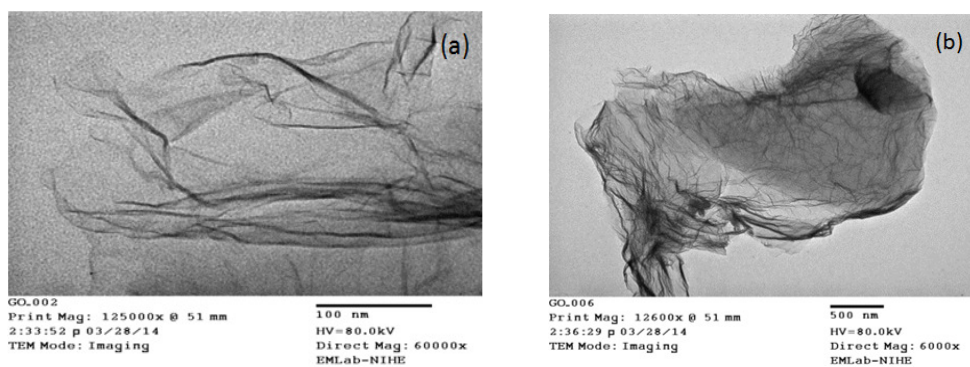


Figure 2. TEM image of graphene oxide (a) and graphene oxide sulfonated (b).

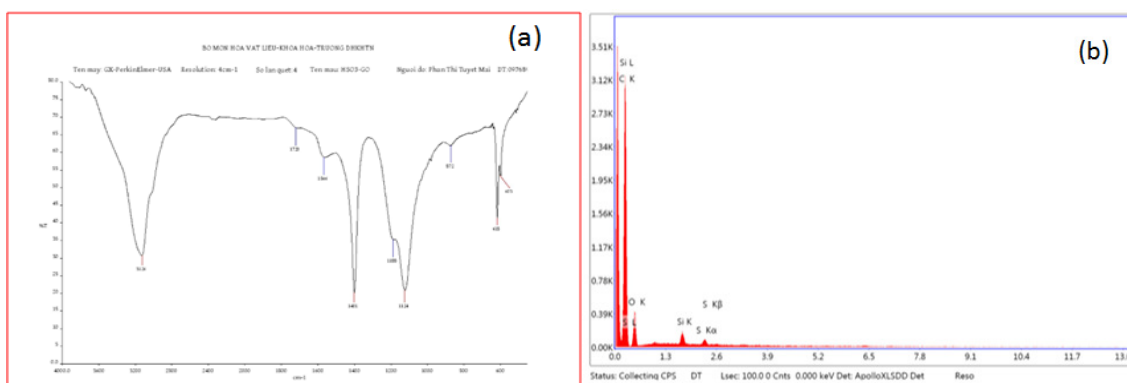


Figure 3. IR (a) and EDS (b) spectrum of GO-SO₃H.

In order to confirm the existence of $-\text{SO}_3\text{H}$ groups in GO sulfonated, EDS spectrum of this catalyst was measured (Figure. 3). The

spectrum showed the presence of sulphur with 0.2% in weight. Hence, it concluded that the sulfonation of GO was successful.

3.2. Catalytic activity

Catalytic activity of GO-SO₃H was evaluated by conversion reaction of fructose to 5-hydroxymethylfurfural. The different parameters were envisaged such as: reaction temperature, reaction time and solvent (fig. 4a, 4b and fig. 5). The results showed that, in DMSO solvent, the HMF yield reached the maximum value of 56% at 120°C. At this reaction temperature, the HMF yield was influenced slightly by reaction time (fig. 4b). This one conforms to the thermodynamics of the reaction, which is an exothermic reaction [8]. Hence, it is not favourable at high temperature. In addition, high temperatures and

long reaction time are favourable for side reactions such as the re-hydration of HMF to form levulinic acid and polymerization to humic acid [9].

The effect of solvent was also envisaged. Instead of DMSO, ethylene glycol (EG) was used as a reaction solvent. The dependence of HMF yield on reaction temperature is represented in figure 6, in EG solvent. It was clear that HMF yield was very low in researched temperature range and reached maximum value 6.4% at 140°C. This low HMF yield may be explained by the interaction of -OH groups in EG molecules with acid groups -SO₃H, which deactivated these catalytic sites (Figure 5).

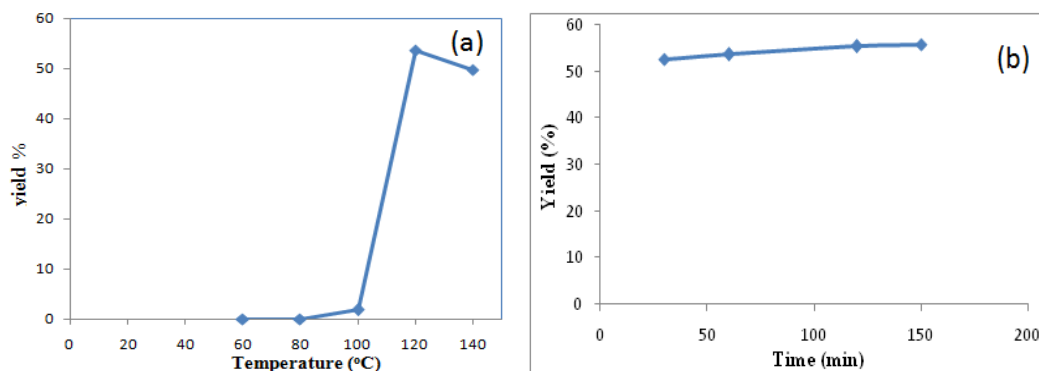


Figure 4. Yield of HMF formation in function of temperature (a) and time (b).

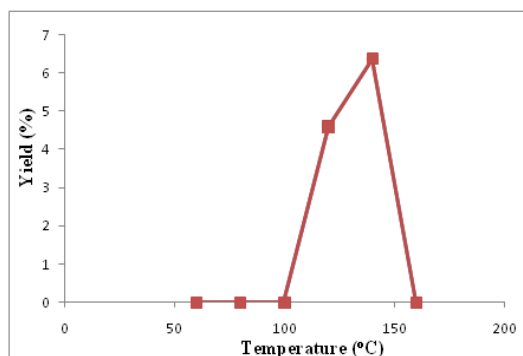


Figure 5. The dependence of HMF yield on reaction temperature (in EG solvent).

4. Conclusions

The results showed the success of synthesis of graphene oxide and its sulfonation. Concretely, XRD patterns indicated a shift of characteristic pick from 26.5° in graphene sample to 10.4° in one of GO. The appearance of two vibrations at 1401 cm^{-1} và 1124 cm^{-1} on the IR spectrum and the presence of 0.2% (wt) sulphur in EDS spectrum proved that the sulfonation process was successful. The various parameters related to the conversion of fructose to HMF have been investigated, such as reaction temperature, reaction time and reaction solvent. In DMSO solvents, HMF yield attained maximum value of 56% at 120°C . It seems that HMF yield didn't depend on the reaction time. This one conforms to the thermodynamics of the reaction, which is an exothermic reaction. Hence, it is not favourable at high temperature. In addition, high temperatures and long reaction time are favourable for side reactions such as the re-hydration of HMF to form levulinic acid and polymerization to humic acid. In EG solvent, the HMF yield was very low, maximum value attained only 6.4% at 140°C . From the results obtained, it clearly showed that

the optimization of sulfonation process is needed to increase the number of active sites in GO-SO₃H catalyst, which improves its catalytic activity.

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Tổng hợp oxit graphen được sunfonic hóa và đánh giá hoạt tính xúc tác của chúng qua phản ứng chuyển hóa fructozơ thành 5-Hydroxymethylfurfural

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Tóm tắt: Oxit graphene (GO) đã được tổng hợp bằng phương pháp Hummer và sulfonic hóa bằng (NH₄)₂SO₄ giải pháp. Các vật liệu thu được được đặc trưng bằng các phương pháp khác nhau như XRD, IR, TEM, EDS. Các kết quả nhiễu xạ tia X cho thấy sự bóc tách thành công graphit với sự dịch chuyển của vị trí cực đại nhiễu xạ từ $2\theta = 26,5^\circ$ của graphit về góc $10,4^\circ$. Các hình ảnh TEM cho thấy

sự tồn tại của tấm graphen oxit với các kích cỡ khác nhau. Sự hình thành nhóm sulfonic ($-\text{SO}_3\text{H}$) trên bề mặt graphene oxit đã được khẳng định bởi phổ IR với sự xuất hiện của peak đặc trưng tại 1401 cm^{-1} và 1124 cm^{-1} ứng với dao động của nhóm S-O và S = O. Hoạt tính xúc tác của GO- SO_3H được đánh giá qua phản ứng chuyển hóa fructozơ thành 5-hydroxymethylfurfural (HMF). Các thông số khác nhau liên quan đến phản ứng (nhiệt độ, thời gian, dung môi), đã được khảo sát. Kết quả cho thấy hiệu suất tạo HMF cao nhất đạt 56% ở điều kiện nhiệt độ phản ứng 120°C , trong 2h và trong dung môi (DMSO).

Từ khóa: Graphen oxit, 5-hydroxymethylfurfural, fructozơ.