



GRAPHENE OXIDE-BASED MATERIALS FOR ELECTROCHEMICAL
HYDROGENATION OF NITRO AND CARBONYL COMPOUNDS IN
MEMBRANE REACTOR AND CATALYSIS OF GLYCEROL ACETYLATION



By
Mr. Itthiporn MOONNEE

A Thesis Submitted in Partial Fulfillment of the Requirements
for Master of Engineering CHEMICAL ENGINEERING
Department of CHEMICAL ENGINEERING
Silpakorn University
Academic Year 2025
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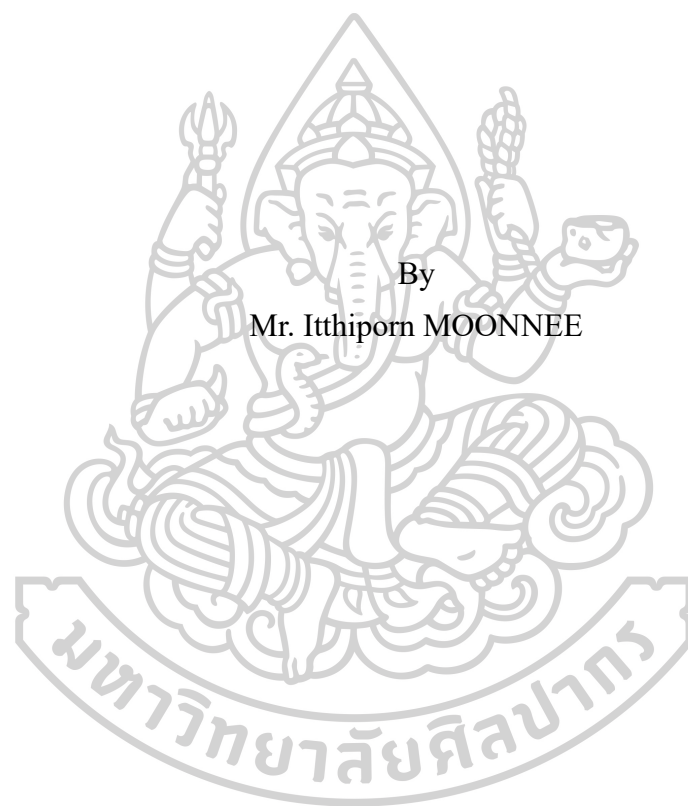
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Title Graphene Oxide-Based Materials for Electrochemical
Hydrogenation of Nitro and Carbonyl Compounds in Membrane
Reactor and Catalysis of Glycerol Acetylation
By Mr. Itthiporn MOONNEE
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Mr. Itthiporn MOONNEE : Graphene Oxide-Based Materials for Electrochemical Hydrogenation of Nitro and Carbonyl Compounds in Membrane Reactor and Catalysis of Glycerol Acetylation Thesis advisor : Associate Professor Worapon Kiatkittipong, D.Eng.

This study investigated graphene oxide (GO)-based materials for sustainable catalytic and electrochemical applications. Two systems were developed: a GO-based proton-conductive membrane reactor for electrochemical hydrogenation, and a sulfonated GO (s-GO) solid acid catalyst for glycerol acetylation. In the electrochemical reactor, the dual-functionalized CeIm-GO membrane exhibited improved proton conductivity and high ion selectivity, enabling energy-efficient hydrogenation under ambient pressure and temperature. Selective reductions of aromatic nitro and ketone compounds were accomplished, highlighting the potential of GO-based membranes for hydrogen-related applications. Simultaneously, pristine GO and s-GO were synthesized and evaluated for glycerol acetylation. Although GO already showed high intrinsic catalytic activity due to its oxygen-containing functional groups, sulfonation introduced $\text{-SO}_3\text{H}$ groups that provided stronger Brønsted acidity and led to modest improvements in selectivity toward diacetin and triacetin while maintaining nearly identical total conversion. The s-GO catalyst showed good short-term recyclability, with deactivation primarily associated with partial loss of sulfonic groups and reduced surface area, while the GO framework remained stable. Overall, this work demonstrates the multifunctionality of graphene oxide as a tunable carbon-based platform. Its adjustable surface chemistry, acidity, and membrane properties position GO-derived materials as promising candidates for green energy conversion, biomass upgrading, and sustainable hydrogen utilization.



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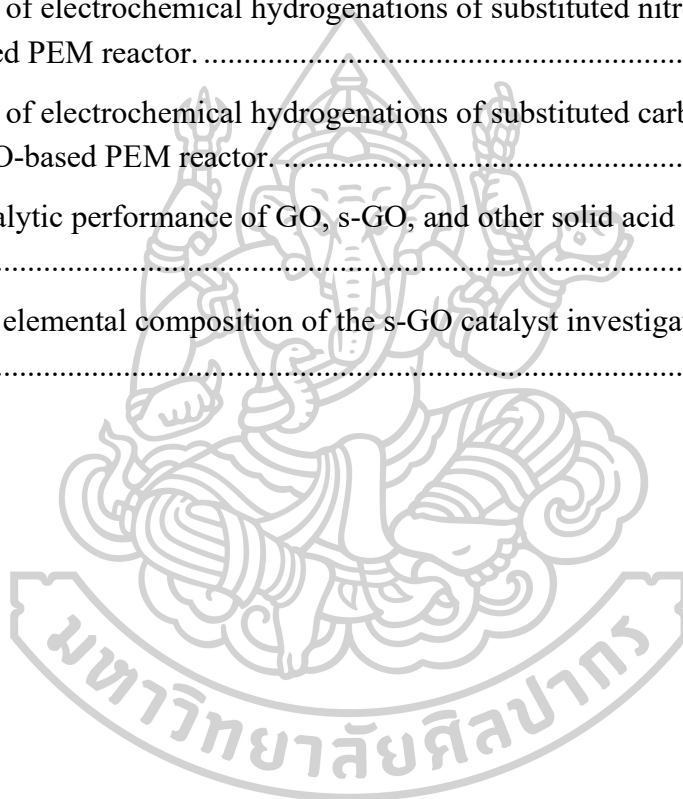


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CHAPTER 1

INTRODUCTION

1.1 Research background

Graphene-based materials have attracted considerable attention due to their remarkable intrinsic properties, such as high specific surface area, superior electrical and thermal conductivities, and exceptional mechanical strengths. Particularly, graphene oxide (GO), one of the graphene derivatives, is composed of various oxygen functionalized groups, (e.g., hydroxyl, epoxy, carbonyl, and carboxyl) on the graphitic plane, along with additional functional groups on the edges. These functionalities make GO a promising material for advanced catalytic and membrane-based applications, including fuel cells, electrochemical reactors, and green synthesis platforms.

Generally, hydrogenation reactions are fundamental transformations in the conversion of unsaturated compounds, playing a crucial role in fine organic syntheses (Lan & Wang, 2020; Qu et al., 2023; Reed-Berendt et al., 2021). The reduction of aromatic nitro compounds into valuable products like aromatic amines, which are necessary intermediates in pharmaceuticals, agrochemicals, and dyes, is essentially dependent on the hydrogenation process (Ahmad et al., 2019; Jagadeesh et al., 2013). Nevertheless, traditional hydrogenation methods often rely on molecular hydrogen under harsh conditions, such as elevated temperatures and high pressures. Furthermore, these methods also require expensive noble metal catalysts (e.g., Pd, Ru, Ir), generating significant costs and raising concerns regarding sustainability, safety, and environmental impact (Cai et al., 2024; Mohanty et al., 2025; Molinari et al., 2016; Nie et al., 2021; Qu et al., 2024; Zhang et al., 2021; Zhao et al., 2025).

To overcome these limitations, a novel approach employing a GO-based proton exchange membrane (PEM) reactor is introduced. This innovative system enables highly selective and additive-free hydrogenation under ambient conditions, offering alternative and sustainable approaches for electrocatalytic hydrogenation of aromatic nitro compounds (Kida et al., 2018; Sahroni et al., 2024). However, pristine GO membranes suffer from structural instability, specifically in humid environments, which hinders their long-term application. Therefore, in this study, the GO membrane

is incorporated with imidazole and doped with cerium ions to improve both stability and proton conductivity. Imidazole moieties facilitate proton transport through a hopping mechanism, while cerium ions enhance the membrane's structural integrity and resistance to degradation. This modified GO membrane is integrated into a PEM reactor architecture, enabling efficient hydrogenation with excellent yields and high selectivity.

Simultaneously, we investigate the catalytic performance of a modified GO catalyst in the acid-catalyzed acetylation of glycerol, a major byproduct of biodiesel production, offering a viable pathway for glycerol valorization (Kaur et al., 2020). Through heterogeneous acid catalysis over a modified-GO catalyst, glycerol can be selectively converted into mono-, di-, and triacetins, which are valuable as fuel additives and in the cosmetic and pharmaceutical industries. Notably, sulfonated GO introduces strong Brønsted acid sites ($-\text{SO}_3\text{H}$ groups) onto the GO surface, which are highly active for acid-catalyzed esterification reactions. These $-\text{SO}_3\text{H}$ groups provide strong protonic acidity, enhancing conversion and selectivity toward acetylated products. Furthermore, GO's large surface area and porosity facilitate better molecular adsorption and increase active catalytic sites, thus improving the reaction kinetics. Therefore, the use of sulfonated GO offers promise as a metal-free, efficient, and environmentally benign alternative to conventional catalytic systems, which suffer from issues such as poor selectivity, high cost, and environmental toxicity.

1.2 Research objectives

This research focuses on the modification and application of GO-based materials for dual functional electrochemical and catalytic purposes, particularly in the field of sustainable chemical processing. The main objectives of this research are as follows:

- i. To synthesize the imidazole-cerium-modified GO membrane with enhanced proton conductivity and stability, and to investigate the feasibility of a synthesized membrane in a PEM reactor for electrochemical hydrogenation of aromatic compounds under room temperature and atmospheric pressure.

- ii. To demonstrate the catalytic performance of sulfonated GO in the acetylation of glycerol, validating it as an efficient, metal-free, and sustainable alternative to conventional acid catalysts.

1.3 Scope of research

Part 1: Electrochemical hydrogenation in a membrane reactor

- 1) GO nanosheets are synthesized via the chemical exfoliation using the modified Tour's method.
- 2) Cerium-imidazole-modified GO (CeIm-GO) membranes are prepared using a vacuum-assisted filtration technique.
- 3) The synthesized membrane is employed in a PEM reactor for electrochemical hydrogenation of aromatic nitro and carbonyl compounds under ambient conditions.
- 4) The hydrogenated products are determined by gas chromatography mass-spectroscopy (GC-MS).

Part 2: Catalysis of glycerol acetylation

- 1) Sulfonated GO (s-GO) are synthesized using a reflux method with controlled amount of concentrated H_2SO_4 .
- 2) Esterification of glycerol is carried out using optimized reaction conditions (1:9 glycerol-to-acetic acid ratio, 5 wt.% catalyst loading, 120 °C, and 2 h).
- 3) The reaction mixtures are analyzed and quantified by high-performance liquid chromatography (HPLC).

CHAPTER 2

FUNDAMENTAL STUDIES

In this study, the modification and utilization of GO-based materials, including electrochemical hydrogenation using a GO-based membrane reactor and the acetylation of glycerol over a modified GO catalyst, are comprehensively discussed. This chapter outlines the fundamental principles and scientific basis of the research, including the following topics:

2.1 Graphene oxide

Graphene and its derivatives are considered noble carbon-based materials that were originally discovered by Geim et al. (Geim, 2009). In particular, graphene oxide (GO), a two-dimensional derivative of graphene, consists of a single atomic layer rich in oxygen-containing functional groups. GO has gained significant attention due to its exceptional chemical versatility, large specific surface area, and outstanding mechanical, electrical, and thermal properties. These attributes render it suitable for diverse applications, such as catalysis, gas sensors, supercapacitors, fuel cells, membranes, and biomedical systems (Ahmad et al., 2024; Chen et al., 2022; Devendran & Nagai, 2023; Suranshe et al., 2023).

2.1.1 Physicochemical properties of GO

The GO structure typically consists of a hexagonal sp^2 and sp^3 hybridized carbon atoms network decorated with abundant oxygen-containing functional groups, such as hydroxyl ($-OH$), epoxy ($-O-$), carbonyl ($C=O$), and carboxyl ($-COOH$), which are distributed across the basal plane and the edges (Yu et al., 2017). These oxygenated groups disrupt the extended π -conjugation of pristine graphene, creating regions of oxidized sp^3 domains interspersed with unoxidized graphitic sp^2 domains. The coexistence of un-oxidized graphitic regions (hydrophobic) and oxygenated domains (hydrophilic) impart amphiphilic properties to GO. This structural heterogeneity enables GO to interact with a wide range of molecules through hydrophobic interactions, hydrogen bonding, electrostatic forces, and π - π stacking. Moreover, the

presence and distribution of functional groups offer versatile opportunities for chemical modification through both covalent and noncovalent interactions, allowing precise tuning of GO's physicochemical behavior for different applications (Choi et al., 2010; Criado et al., 2015; Englert et al., 2011).

GO possesses highly hydrophilic properties due to its abundant oxygen functionalities, enabling excellent dispersibility in water and many polar solvents. This property distinguishes GO from pristine graphene, which is hydrophobic and difficult to disperse without surfactants. The unique two-dimensional structure of GO also provides an exceptionally high specific surface area. Functional groups introduce defects, porosity, and expanded interlayer spacing relative to graphite, collectively exposing more accessible surface area sites and enhancing its reactivity (Hatakeyama, Tateishi, et al., 2014).

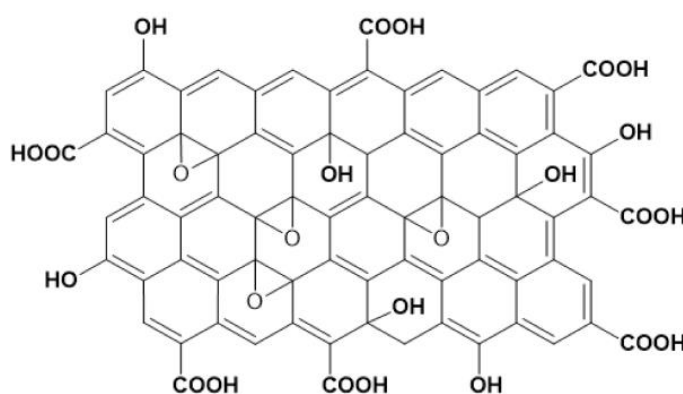


Figure 1 The typical structure of graphene oxide nanosheets, consisting of various oxygen-containing groups on its basal plane and edges.

Generally, GO nanosheets can be derived from graphite through several techniques, such as mechanical exfoliation, chemical exfoliation, thermal reduction, etc., which is known as the top-down method (Moonnee et al., 2024; Sun, 2019). In contrast, GO is produced using minor carbon precursors, involving the carbonization of smaller precursors to form GO. The bottom-up approaches include chemical vapor deposition (CVD), epitaxial growth, and thermal pyrolysis. Commonly, the top-down methods are more practical and straightforward for GO production. One of the most widely used techniques is the chemical exfoliation (i.e., Brodie, Staudenmaier, and

Hummer's method), in which graphite is intercalated with H_2SO_4 and NaNO_3 , followed by chemically oxidized with strong oxidizing agents, like KMnO_4 (Brodie, 1859; Hummers & Offeman, 1958; Staudenmaier, 1898). During this process, various oxygenated functional groups are incorporated into graphitic plane, resulting in the formation of graphite oxide. Subsequently, graphite oxides are further exfoliated by ultrasonication to obtain a single layer GO nanosheets. In 2010, the improved synthesis was reported by Tour et al., replacing NaNO_3 with H_3PO_4 which causes the generation of toxic gas. Most importantly, this improved method essentially provides a higher yield GO with greater oxidation state, emphasizing its large-scale production (Marcano et al., 2010).

Table 1 Physical properties of graphene oxide synthesized by different synthesis methods (Moonnee et al., 2024).

Method	Specific surface area (m^2/g)	C/O ratio	Interlayer distance ($\text{\AA}^\circ$)
Brodie	200–550	1.6–2.9	6.4–7.2
Staudenmaier	1500–1800	2.5–3.1	6.8
Hummers	130–1500	0.9–2.8	7.2–8.6
Tours	70–800	0.7–1.3	7.9–9.1

Overall, the synthesis methods significantly influence the structural, mechanical and electrical properties of GO. During this process, oxygen functionalities are incorporated, determining the final structure, acidity, and surface chemistry of GO. Subsequently, the exfoliation process results in single-layer or few-layer nanosheets with tunable physicochemical properties.

2.1.2 Proton conduction in GO membrane

Due to the presence of oxygenated functional groups, GO possesses a remarkable proton conductivity, which refers to its ability to facilitate the proton (H^+) transport. These oxygen functional groups, such as hydroxyl, epoxy, carbonyl, and carboxyl, establish a complex network within GO nanosheets. Interestingly, the spacing between interlayers caused by these functional groups (approximately 0.76 nm) greatly

facilitate the proton conduction through the GO structure, in which ionic species can effectively transport both horizontally (in-plane) and vertically (through-plane) (Karim et al., 2016). In this configuration, the proton conduction mechanisms in GO can be categorized into two mechanisms. Firstly, the Grotthuss mechanism, also known as proton hopping, involves protons hop along the hydrogen bond networks, caused by negatively charged oxygenated functionalities, facilitating in-plane conductivity of proton (Zhang et al., 2022). Meanwhile, protons can diffuse in water in the form of hydronium ions (H_3O^+), which is known as the vehicle mechanism. It is noteworthy that the proton conductivity of GO is comparable to that of Nafion, a widely used commercial PEM known for its high proton conductivities (from 0.01 to 0.1 S cm^{-1}) under humid conditions. These outstanding proton conduction properties make GO-based membranes suitable as a solid-state electrolyte for advanced electrochemical applications, such as batteries, sensors, supercapacitors, and fuel cells (Hatakeyama, Tateishi, et al., 2014).

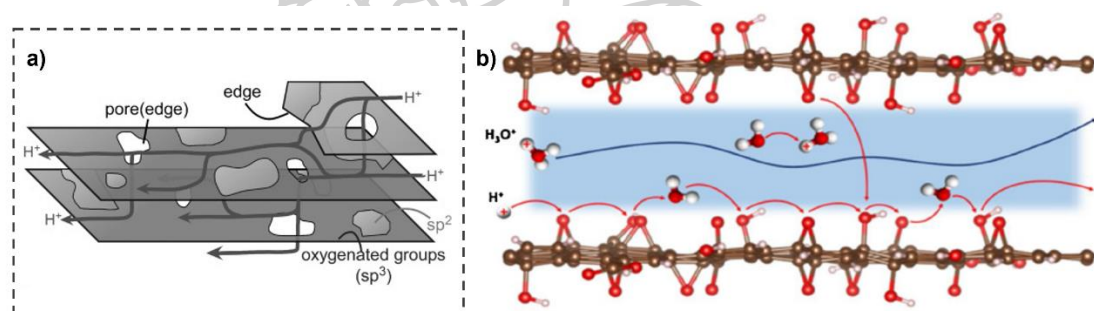


Figure 2 a) Proposed mechanism for proton conductivity in multilayer GO (Hatakeyama, Karim, et al., 2014). b) Proton conduction through GO membranes, including the Grotthuss and vehicle mechanism (Bayer et al., 2016).

2.2 Proton exchange membrane reactor

A proton exchange membrane (PEM) reactor, also known as a membrane reactor, is an electrochemical device employed in electrosynthetic applications, specifically hydrogenation, utilizing a proton-conducting polymer electrolyte membrane. The membrane selectively transports protons generated at the anode, while blocking electrons and most other ions. Electrons travel via an external circuit, meeting protons again at the cathode where the desired electrochemical reaction occurs. This physical

separation of charge carriers allows precise control over reaction pathways and effectively isolates reactants and products, simplifying downstream separation and improving safety. A typical PEM reactor requires a membrane electrode assembly (MEA), which consists of the PEM sandwiched between catalyst layers on both sides. This architecture ensures efficient proton transport, good electrical conductivity, and high interfacial catalytic activity. Owing to these characteristics, PEM reactors have emerged as powerful and potential platforms for several organic transformations these days (Green et al., 2012).

In proton exchange membrane fuel cells (PEMFCs), hydrogen oxidation occurs at the anode, producing protons and electrons. Consequently, protons migrate across the hydrated membrane, while electrons flow through the external circuit. At the cathode, oxygen reduction reaction (ORR) occurs, forming water. This system directly converts chemical energy into electricity with high efficiency and low environmental impact (Üregen et al., 2017). Membrane hydration, morphology, and interfacial nanostructure strongly influence proton conductivity, mechanical stability, and overall device durability. Typically, the system operates at moderate temperatures and relies on Platinum-based catalysts due to their activity toward hydrogen oxidation and oxygen reduction.

Beyond energy applications, PEM systems can function as selective membrane reactors for chemical synthesis. By facilitating product removal or enabling proton-specific transfer, PEM reactors improve reaction equilibrium, enhance selectivity, and minimize side reactions, making them attractive for green organic transformations and fine chemical production.

2.3 Electrocatalytic hydrogenation

Hydrogenation is one of the most essential transformations in organic chemistry because of its wide substrate scope, excellent yields, and industrial scalability (Rader & Smith, 1962). Conventionally, hydrogenation involves the addition of molecular hydrogen to unsaturated functionalities such as C=C, C≡C, C=O, and nitro groups in the presence of a metal catalyst. Electrochemical hydrogenation (ECH) offers a more sustainable alternative by replacing pressurized molecular hydrogen with electrochemically generated hydrogen atoms. This process is typically carried out in a

proton exchange membrane reactor, where the membrane separates the anodic and cathodic compartments, ensuring selective proton transport and preventing undesired oxidation reactions (Han et al., 2024). Compared with thermal hydrogenation, ECH offers the key advantages including; (i) operation under mild conditions (ambient temperature and pressures), (ii) elimination of H₂ storage and handling, (iii) enhanced selectivity derived from controlled proton-electron transfer process, (iv) tunable product distribution through applied voltage and current density, and (v) compatibility with green electricity, contributing to decarbonized chemical manufacturing (Liu et al., 2023; Mitsudo et al., 2024; Takano et al., 2016).

2.3.1 Fundamental electrocatalytic hydrogenation mechanism

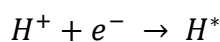
The electrocatalytic hydrogenation mechanism involves the sequential delivery, reduction, and reaction of protons on the catalyst surface. The process can be described through three key steps (Sherbo et al., 2019):

1) Proton generation and migration

At the anode, water oxidation or hydrogen oxidation generates proton (H⁺). These protons migrate toward the cathode either through an electrolyte solution or a proton-conducting membrane, depending on reactor configuration. The ability to deliver protons efficiently and selectively is essential for achieving high hydrogenation activity.

2) Formation of adsorbed hydrogen atoms (H^{*})

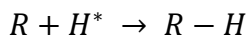
At the cathode surface, protons accept electrons and are reduced to reactive adsorbed hydrogen species (H^{*}) on the metal catalyst surface:



Metal catalysts such as Pt, Pd, Ni, and Ru are commonly employed due to their ability to adsorb and activate hydrogen species. The binding energy of hydrogen on the catalyst significantly influences reactivity; metals with appropriate hydrogen adsorption strength tend to show higher hydrogenation performance.

3) Hydrogenation of organic substrates

Organic molecules (R) adsorb onto the catalyst surface and react with the adsorbed hydrogen atoms to form hydrogenated products:



Depending on substrate structure, the process may involve multiple hydrogenation steps. For example, nitro compounds undergo stepwise reduction to anilines, carbonyl compounds are reduced to alcohols, and alkenes and alkynes are converted to alkanes. Selectivity is governed by the substrate's adsorption mode, surface coverage of hydrogen, catalyst properties, and the applied potential.

In the hydrogenation of nitro or carbonyl compounds, the interaction between proton availability, catalyst composition, and membrane properties determines activity and selectivity. In this study, the GO membrane modified with imidazole and cerium enhances proton conductivity while suppressing undesired anion crossover. This ensures that protons efficiently reach the cathodic compartment, where substrates such as nitrobenzene and acetophenone are selectively reduced to their corresponding aniline and phenylethanol, respectively. The tailored membrane environment also minimizes competitive reactions such as hydrogen evolution reaction (HER), improving Faradaic efficiency and product selectivity.

2.4 Acetylation of glycerol

2.4.1 Glycerol and its valorization

Glycerol (propane-1,2,3-triol) is a polyhydric alcohol containing three hydroxyl (–OH) groups, which makes it highly hydrophilic and chemically reactive. Over the past several years, the rapid expansion of biodiesel production through transesterification has resulted in a large surplus of crude glycerol, typically accounting for around 10% of the total biodiesel output. This oversupply has consistently exceeded market demand, causing a significant decline in the economic value of glycerol (Farobie & Matsumura, 2017). As a result, considerable research efforts have focused on developing sustainable and high-value utilization pathways that can efficiently convert glycerol into value-added chemicals. A variety of chemical transformations have been explored for glycerol valorization, as summarized in Figure 3 (Cecilia et al., 2019; Gonçalves et al., 2008). Among these routes, acetylation has emerged as a promising strategy for glycerol conversion. In this process, glycerol reacts with acetic acid or

acetic anhydride to form glycerol acetates, collectively known as acetins, through catalytic esterification.

The acetylation products include glycerol monoacetate (monoacetin), glycerol diacetate (diacetin), and glycerol triacetate (triacetin). These differ in the number of acetyl groups substituting the hydroxyl groups on the glycerol backbone (Chandrakala et al., 2014). Each acetin possesses distinct physicochemical properties and industrial applications. For example, monoacetin is widely used in plasticizers, cosmetics, pharmaceuticals, and food additives (Wypych, 2013). Diacetin serves as a solvent and an intermediate in fine chemical synthesis. Triacetin is particularly important as a fuel additive, improving ignition quality, cold flow properties, and combustion characteristics in biodiesel blends (Chozhavendhan et al., 2020). Thus, the transformation of crude glycerol into these value-added chemicals not only enhances its economic value but also contributes to waste reduction and resource efficiency, supporting the development of sustainable biorefinery systems.

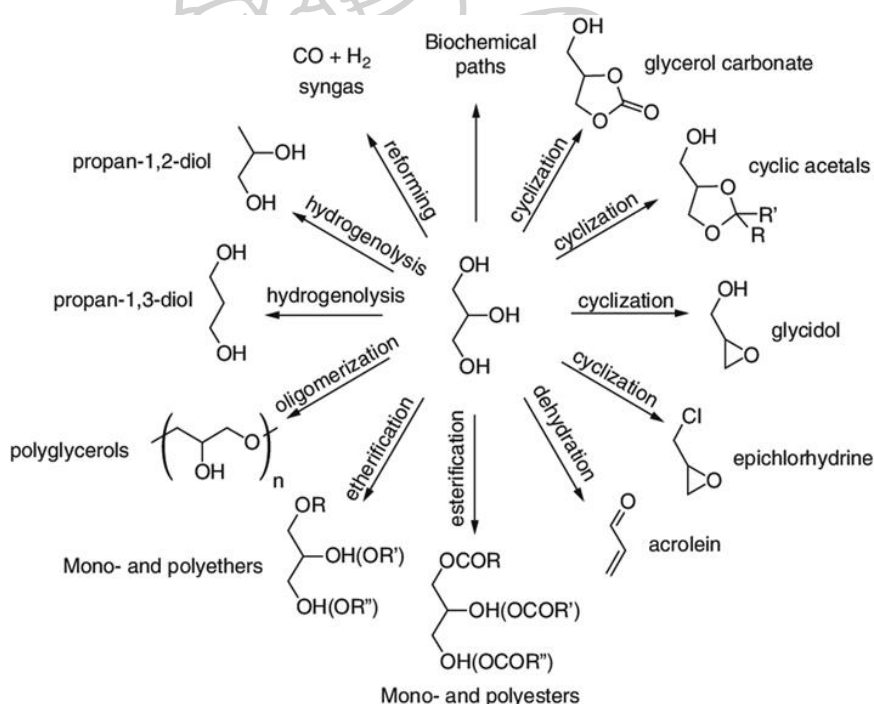
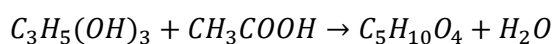


Figure 3 Recent advances on the valorization of glycerol (Cecilia et al., 2019).

2.4.2 Acetylation reaction mechanism

The acetylation of glycerol proceeds via an acid-catalyzed esterification reaction, involving the substitution of the hydroxyl hydrogen atoms in glycerol backbone with acetyl groups derived from acetic acid or acetic anhydride. The reaction mechanism consists of three consecutive esterification steps, including the formation of monoacetin, diacetin, and triacetin, respectively:



In the first step, glycerol rapidly reacts with equimolar of acetic acid to form monoacetin. This step requires relatively low activation energy due to the abundance and accessibility of hydroxyl sites on glycerol. Consequently, monoacetin undergoes further esterification with acetic acid to yield diacetin. Triacetin is finally generated by esterification of diacetin with additional acetic acid. Essentially, the second and third steps occur more slowly because partial acetylation both increases steric hindrance around the remaining hydroxyl groups and reduces their nucleophilicity. Since each esterification is reversible and equilibrium-limited, the reaction typically requires either an excess of acetic acid or continuous removal of produced water to drive the system toward the formation of higher acetins, particularly triacetin. The overall reaction pathway is illustrated in Figure 4 (Shera Farisya et al., 2021).

The decreasing reaction rate in the later stages highlights the importance of catalyst selection, reaction conditions, and water management in optimizing glycerol acetylation. Efficient catalysts and appropriately engineered reaction environments can shift the equilibrium, enhance selectivity, and improve the overall yield of desired acetylation products.

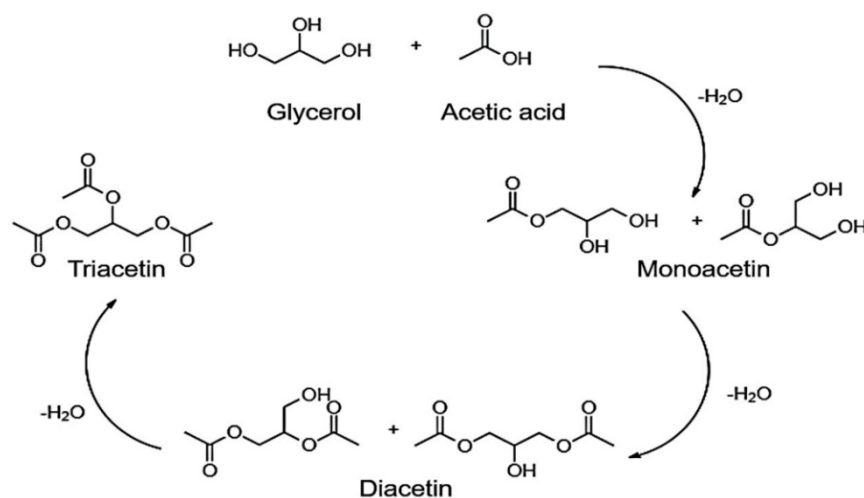


Figure 4 Reaction pathway of glycerol esterification with acetic acid, which derives monoacetin, diacetin, and triacetin (Shera Farisya et al., 2021).

2.5 Literature reviews

This section summarizes the relevant scientific background and previous studies that support the development of functionalized graphene oxide materials for electrochemical hydrogenation and catalytic glycerol acetylation. The review begins with the fundamental properties of graphene oxide and its advantages as a tunable two-dimensional material. It then discusses reported methods of GO functionalization, including heteroatom doping, metal-ion coordination, and sulfonation. Key findings from previous studies on GO-based proton-conductive membranes and GO-derived solid-acid catalysts are highlighted. Finally, recent progress in electrochemical hydrogenation and glycerol acetylation is examined to identify current challenges and research gaps addressed in this thesis.

2.5.1 Enhanced proton conductivity of GO membranes

GO membranes have drawn significant attention as promising solid-state electrolytes in electrochemical applications due to their abundant oxygenated functional groups, high water uptake capacity, and tunable interlayer spacing. These features contribute to their intrinsic proton conductivity, which is strongly dependent on environmental humidity. The hydrophilic nature of GO allows it to form hydrogen-

bond networks that facilitate proton hopping, according to the Grotthuss mechanism, especially under humid conditions.

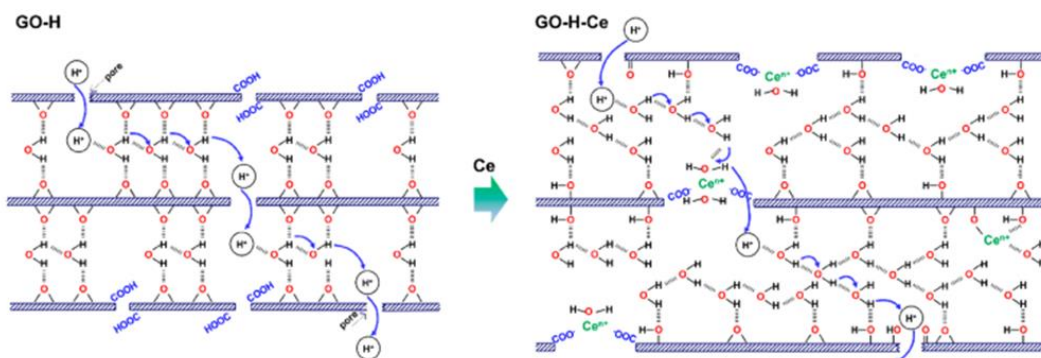


Figure 5 Proposed mechanism of Ce ions intercalating into GO membranes, enhancing proton conduction through GO nanosheets (Hamidah et al., 2020).

To further improve the proton conductivity and durability of GO membranes, various modification strategies have been explored. These include heteroatom doping, polymer blending, and ionic cross-linking. For example, incorporating GO with metal cations has emerged as an effective strategy to improve both proton conduction and membrane robustness. According to Hamidah et al. demonstrated that intercalation of cerium ions ($\text{Ce}^{3+}/\text{Ce}^{4+}$) into GO nanosheets significantly increased proton conductivity and water stability (Hamidah et al., 2020). Cerium ions interacted with oxygen-containing groups, especially carboxyl and epoxide groups, on the GO surface, forming a three-dimensional coordination network. This Ce-assisted expansion of interlayer spacing not only facilitated the hydration of internal layers but also enhanced the formation of proton-conductive pathways. The resulting self-standing GO–Ce membranes exhibited proton conductivities of $2.8 \text{ mS}\cdot\text{cm}^{-1}$ at room temperature, which is comparable to commercial Nafion membranes.

2.5.2 Electrochemical hydrogenations using a PEM reactor

Electrocatalytic hydrogenation using a PEM reactor has emerged as a green alternative to traditional thermocatalytic hydrogenation, which often involves hazardous hydrogen gas, elevated temperatures, and noble metal catalysts. In contrast, PEM reactors allow localized proton delivery, minimizing over-reduction and

improving selectivity. For instance, Takano et al. demonstrated the electrocatalytic hydrogenation of toluene to methylcyclohexane in a Nafion-based PEM reactor, achieving high current efficiencies under mild conditions with PtRu/C catalysts (Takano et al., 2016). However, the system suffered from performance drops at higher current densities, primarily due to competing HER and membrane dehydration. This limitation highlighted the need for alternative membrane materials with improved water retention and selective proton transport.

Recent advancements have reported that GO membranes, an oxygenated derivative of graphene, exhibits remarkable proton conductivity due to the presence of oxygen-containing functionalities. Ahmad et al. reported a GO-based PEM reactor for the hydrogenation of alkynes and alkenes (Ahmad et al., 2025). This system demonstrated superior selectivity (up to 93%) under ambient conditions, without requiring pressurized hydrogen or added reducing agents. Interestingly, the intercalated Ce ions further stabilized the interlayer arrangement, maintaining consistent proton transport pathways during operation. Meanwhile, Sahroni et al. extended the use of a GO-based PEM reactor to the electrochemical deuteration of organic substrates, particularly for pharmaceuticals (Sahroni et al., 2024). By replacing water with D₂O as the deuterium source. The reactor enables selective and isotopically deuterations under mild, metal-free conditions. Moreover, the reactor design allowed for the effective separation of proton generation and substrate hydrogenation, reducing byproduct formation and catalyst contamination.

These findings have direct implications for the electrochemical hydrogenation of nitro compounds. Nitroaromatics, such as nitrobenzene, are typically reduced via multistep electron-proton transfer mechanisms, which benefit from stable, efficient proton delivery and localized hydrogenation environments. These characteristics of GO, including high proton conductivity, chemical tunability, and chemical tunability, make it an ideal material for PEMs with selective and efficient reduction of nitro and ketone compounds.

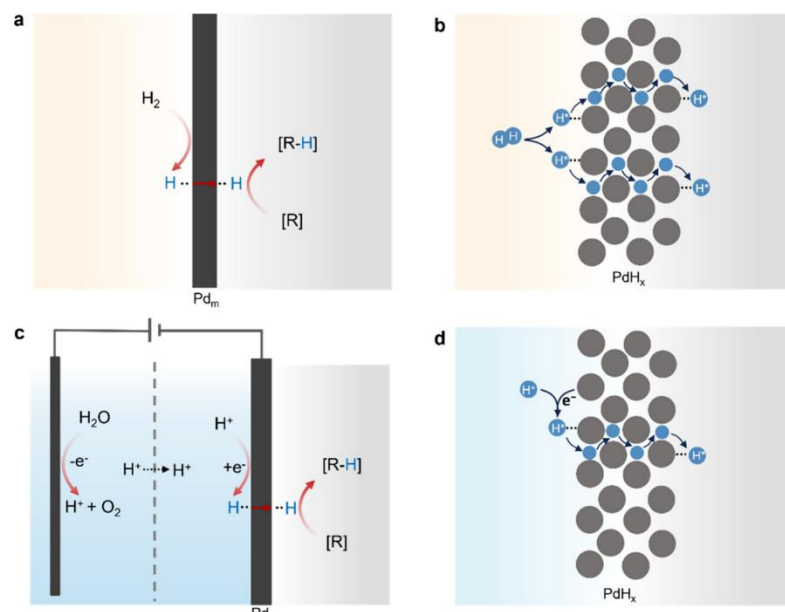


Figure 6 Simplified schematic diagram for the hydrogenation of an organic substrate (R) using (a, b) hydrogen gas as the hydrogen source and (c, d) protons from water as the hydrogen source (Han et al., 2024).

2.5.3 Glycerol acetalization over heterogeneous catalyst

The global expansion of biodiesel production has resulted in a significant surplus of glycerol, prompting extensive research into catalytic valorization strategies. Among these, the acetylation of glycerol has gained wide attention due to its ability to convert low-value crude glycerol into commercially valuable acetins (monoacetin, diacetin, and triacetin). These acetylated derivatives exhibit diverse industrial applications: monoacetin serves as a plasticizer and emulsifier; diacetin is used in cosmetics and fine chemical synthesis; and triacetin is a high-performance additive for improving the ignition and cold-flow properties of biodiesel blends. However, the esterification between glycerol and acetic acid is intrinsically slow and thermodynamically limited, requiring catalysts to enhance conversion and direct selectivity toward higher acetins (Gonçalves et al., 2008).

Traditionally, homogeneous mineral acids such as H₂SO₄, HCl, and p-toluenesulfonic acid (PTSA) have been employed due to their strong acidity and high catalytic efficiency. Despite outstanding activity, these catalysts pose several drawbacks, including equipment corrosion, hazardous waste generation, low selectivity, and extensive purification steps to separate the catalyst from the products.

These limitations have shifted research interest toward heterogeneous solid acid catalysts, which offer advantages such as recyclability, reduced environmental impact, ease of catalyst–product separation, and compatibility with continuous flow systems. (Shera Farisya et al., 2021).

A wide variety of heterogeneous catalysts have been investigated for glycerol acetylation, each offering distinct advantages and limitations (Table 2). Ion-exchange resins such as Amberlyst-15 provide strong Brønsted acidity and good catalytic activity, although their thermal instability and susceptibility to deactivation in the presence of water can restrict long-term use (Gonçalves et al., 2008; Zhou et al., 2013). Zeolites, known for their well-defined microporous frameworks and shape-selective behavior, can offer high selectivity but often suffer from diffusion limitations due to their small pore size, which hampers the access of bulky reactants like glycerol (Ferreira et al., 2009; Kirumakki et al., 2006; Kong et al., 2016). Metal oxides, including ZrO_2 , TiO_2 , and Nb_2O_5 , have also been explored for their solid acidity and chemical robustness; however, these materials sometimes require elevated temperatures or extended reaction times to achieve high triacetin yields (Lauriol-Garbey et al., 2011). Sulfated metal oxides such as $\text{SO}_4^{2-}/\text{ZrO}_2$ combine both Brønsted and Lewis acidity and exhibit high initial activity, yet they may experience sulfate leaching, leading to loss of catalytic performance over repeated cycles (Rat et al., 2008; Shera Farisya et al., 2021).

Although these catalysts show potential, many suffer from inherent drawbacks including insufficient surface area, hydrophobic surfaces leading to poor glycerol adsorption, limited accessibility of acid sites, and decreased activity upon recycling. These challenges highlight the need for structurally adjustable, high surface area, and hydrophilic solid acid catalysts.

2.5.4 Acid-catalyzed esterification over GO

In this context, GO has emerged as a promising catalytic material for glycerol acetylation due to its unique two-dimensional structure, high dispersibility, and abundance of oxygen-containing functional groups. These groups, including hydroxyl, epoxide, carbonyl, and carboxyl functionalities, act collectively as Brønsted and Lewis acid sites, enabling activation of acetic acid and enhancing nucleophilic attack by

glycerol. Unlike conventional solid acids that often suffer from low hydrophilicity, GO exhibits strong affinity for polar reactants, allowing more effective surface interactions and improved reaction kinetics (Hou et al., 2016). Recent studies have demonstrated the potential of GO-based catalysts in esterification reactions. Recent studies have demonstrated the potential of GO-based catalysts in esterification reactions. Hidayati et al. (2024) synthesized GO by oxidizing multi-walled carbon nanotubes (MWCNTs) using a modified Hummers' method and applied it to glycerol acetylation. Despite a reduction in surface area after oxidation, the introduction of oxygenated groups significantly increased overall acidity (1.55 mmol/g), leading to excellent catalytic performance. The catalyst achieved a high glycerol conversion of 93.04%, with a favorable distribution of monoacetin (47.65%), diacetin (29.21%), and triacetin (23.36%). This demonstrates that in GO-based systems, acid site density and chemical functionality often play a more crucial role than physical surface area, distinguishing GO from many metal-oxide catalysts where surface area is the main determinant of activity (Hidayati et al., 2024).

Other carbon-based solid acid catalysts were also reported by Prasad and colleges (Chandrakala et al., 2014). The triacetin synthesis using a sustainable two-step methodology over solid acid catalysts derived from glycerol was investigated. The catalyst was prepared through simultaneous carbonization and sulfonation of glycerol using H_2SO_4 , resulting in high acid site density (1.6 mmol/g) The first step involved acetylation with acetic acid (1:4 molar ratio), followed by a second step using acetic anhydride. Under optimized conditions, the process achieved 100% glycerol conversion and 100% selectivity to triacetin. Notably, the catalyst was reusable over five cycles without significant loss of activity, confirming its robustness.

Table 2 Comparison of acetylation of glycerol over different solid-acid catalysts (Zhou et al., 2013).

Catalyst	Reaction parameters			X_G (%)	Selectivity (%)	
	MR	Temp (C)	Time (min)		DAG	TAG
Amberlyst 15-1	9:1	110	270	97.1	47.7	44.5
HZSM-5				85.6	25.7	7.7

HUSY				78.4	20.6	5.6
Amberlyst 35	6:1	105	240	99.0	-	25.9
HY				80.9	-	3.2
PMo immobilized NaUSY zeolite	15:1	-	180	68	59	2
Sulfonic acid- modified SBA-15	9:1	125	240	90	85	
(DAG+TAG)						

MR = molar ratio; X_G = glycerol conversion

Among emerging materials, sulfonated GO has received particular attention. By introducing $-\text{SO}_3\text{H}$ groups onto the GO surface, the material gains strong Brønsted acidity while preserving its high dispersibility and two-dimensional structure. Sulfonation significantly enhances the proton-donating ability of the catalyst, thereby promoting triacetin formation. Moreover, the stability, metal-free nature, and tunable chemistry of sulfonated GO make it an environmentally friendly alternative to traditional solid acids. Thus, in the present study, sulfonated GO is systematically investigated as a sustainable catalyst for glycerol acetylation, aligning with green chemistry principles and demonstrating potential for industrial application.



CHAPTER 3

RESEARCH METHODOLOGY

This chapter provides the details of experimental procedures of electrochemical hydrogenation in a PEM reactor (e.g., GO synthesis, membrane fabrication, material characterization, electrochemical hydrogenation) and catalytic esterification of glycerol (e.g., catalyst preparation, catalyst characterization, catalytic activity measurement, and recyclability test).

3.1 Electrochemical hydrogenation in a GO-based membrane reactor

3.1.1 Chemical and materials

All reagents in this work were purchased and used without further purification. Deionized water was used throughout the experiments. Imidazole ($\geq 99\%$), nitrobenzene ($\geq 99\%$), p-nitrophenol ($\geq 99\%$), nitrotoluene ($\geq 99\%$), 1-methoxy-4-nitrobenzene ($\geq 98\%$), and 4-methoxyacetophenone ($\geq 99\%$), were obtained from Tokyo Chemical Industry Co., 4-chloroacetophenone ($\geq 98.5\%$), acetophenone ($\geq 95\%$), Sodium formate (98%), Potassium permanganate ($\geq 99\%$), hydrochloric acid (37%), phosphoric acid (85%), sulfuric acid ($\geq 95\%$), hydrogen peroxide (35%), cerium (IV) sulfate tetrahydrate (99.5%) were purchased from Wako Pure Chemical Industries, Ltd., Graphite was obtained from Ito Graphite, Kuwana, Japan. Solvents were obtained from commercial sources.

3.1.2 Synthesis of graphene oxide

GO is synthesized via the modified Tour's method, involving the chemical oxidation and followed by the exfoliation (Marcano et al., 2010). As shown in Figure 7, expanded graphite (3.0 g) with median diameter of 5-50 μm was mixed with 18 g of potassium permanganate. The mixture was added with a total of 400 mL of an acidic solution, containing H_2SO_4 and H_3PO_4 (9:1). Consequently, the mixture was homogeneously stirred in an oil bath that heated up to 50 C. After stirring for 12 h, the mixture's color turned purple brown, suggesting complete oxidation. Subsequently, the mixture was cooled down to room temperature while distilled water (400 mL) was

added slowly. To terminate the oxidation reaction, 30 mL of H_2O_2 was added to the beaker until the color turned brown yellowish. After cooling, the solid products were recovered by centrifugation at 4000 rpm for 15 minutes while washed with an aqueous of 5% HCl three times, followed by distilled water three times. Finally, the precipitate was collected and exfoliated by ultrasonication for 12 h to obtain the GO suspension.

3.1.3 Membrane fabrication

Imidazole-cerium-doped GO membranes were prepared by intercalating 0.005 mmol of cerium (IV) sulfate (2.0 mg) with a GO suspension (4.99 mg/mL). Subsequently, imidazole (0.5 mmol, 68 mg) was dissolved in distilled water (5.0 mL) and sonicated for 15 min to ensure complete dissolution. The imidazole solution (0.1 M) was added to the prepared Ce-GO suspension under continuous stirring for 2 h. Following the mixing step, the ImCe-GO membranes were fabricated by vacuum filtration using two stacked filtered membranes with pore diameters of 45 and 180 μm as supporting membranes. The average thickness of final membrane was approximately 45 μm .

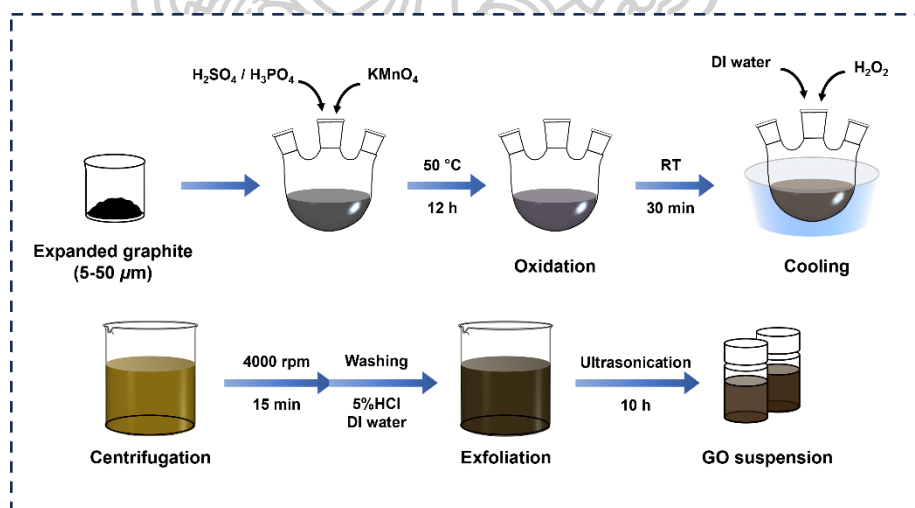


Figure 7 An illustration of GO synthesis via a modified Tour's method, using expanded graphite as a precursor.

3.1.4 Membrane characterizations

The interlayer distance between nanosheets of the GO membrane was analyzed by X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 0.154$ nm, $U = 40$ kV, and $I = 15$ mA)) in the 2θ range of 5° - 60° (MiniFlex 600, Rigaku). Fourier transform infrared (FTIR 4100, JASCO) spectroscopy using an attenuated total reflectance (ATR) method was employed to examine the functional groups presented on the membrane in the wavelength between 600 and 4000 cm^{-1} . To confirm the presence of functionalities, X-ray photoemission spectroscopy (XPS, PerkinElmer) was carried out using a PHI 1600 system. The morphology and structure of the membranes was observed using field-emission scanning electron microscopy (SEM; JSM7600F, JEOL). In addition, energy dispersive X-ray spectroscopy (EDS) was used to determine the elemental composition and mapping on the membranes. The mechanical stability of membranes was measured by immersing them in distilled water for 30 days.

3.1.5 Proton transport number and conductivity measurement

The proton transfer number of the GO membrane was evaluated using a concentration cell setup. A membrane coated on both sides with Pt/C was mounted in a custom-designed glass cell, as shown in Figure 8. Platinum mesh electrodes were placed on either side of the membrane and connected to a precision electrometer (Keithley 2100, Keithley Instruments, USA). One side of the membrane was continuously exposed to 5% H_2 balanced with Ar, while the opposite side was exposed to varying H_2 concentrations (1-5% in Ar). Both gas streams were maintained at a constant flow rate of 100 mL/min.

Proton conductivity was assessed through electrochemical impedance spectroscopy (EIS) using an impedance analyzer (1260, Solartron) over a frequency range of 1 Hz to 1 MHz, with an applied AC amplitude of 10 mV. Proton conductivity (σ) was determined from the following equation:

$$\sigma = \frac{L}{RA} \quad (1)$$

Where σ (S cm^{-1}) is the conductivity, L (cm) is the membrane thickness, R (Ω) is the measured bulk resistance, and A (cm^2) is the electrode area.

Additional I-V measurements were conducted to determine total electrical conductivity using a potentiostat (Interface 1000, Gamry Instrument).

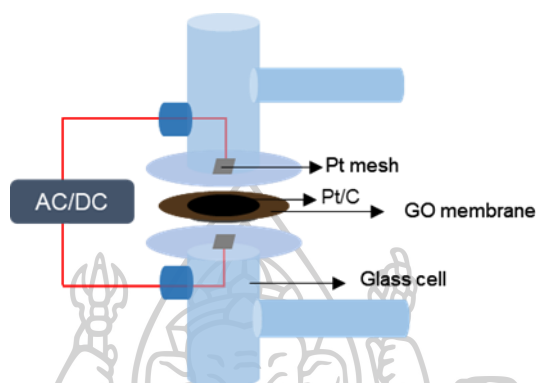


Figure 8 Schematic diagram of proton conductivity measurement.

3.1.6 General procedure for electrochemical hydrogenation

The PEM reactor for electrochemical hydrogenation of nitrobenzene and nitrobenzene derivatives was designed and assembled using two carbon plates as electron collectors, which connect a gas inlet and outlet to the membrane where protons were reduced at the membrane surface. Initially, the membrane was coated with Pt/C catalyst on both sides of the membrane by deposition technique and was sandwiched by two carbon plates, as shown in Figure 9. Subsequently, the anode and cathode side of the electrochemical cell were connected to a potentiostat to apply a constant current density.

Nitrobenzene (0.5 mmol) was dissolved in ethanol (10 mL). Hydrogen gas (1-5% H_2 in humidified Ar) was passed through a bubbler containing 1 M H_2SO_4 at a flow rate of 100 mL/min and introduced into the anode chamber of the reactor. The reaction was carried out at room temperature under constant current densities for 24 h. After completion, the reaction mixture was collected and filtered using a 45 μm pore-diameter PTFE membrane.

The hydrogenation products were analyzed by gas chromatography-mass spectroscopy (GC-MS, Shimadzu Corporation) using an HP-5MS capillary column

(0.25 mm diameter $\times$ 30 m length), where helium gas was used as the carrier gas. The temperature was programmed to increase from 50 °C to 280 °C at a rate of 20 °C/min. Product concentrations were determined using the internal standard method with *n*-decane as an internal standard.

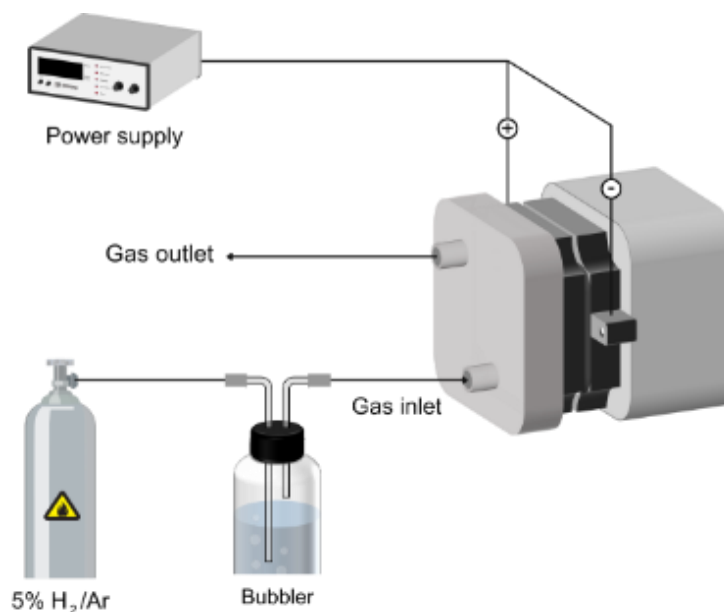


Figure 9 Schematic of electrochemical hydrogenation in a GO-based proton exchange membrane reactor.

3.2 Acetylation of glycerol over a modified GO catalyst

3.2.1 Chemicals and Materials

All reagents in this work were purchased and used without further purification. Deionized water was used throughout the experiments. Glycerol monoacetate ($\geq 98\%$) was purchased from Thermo Fisher scientific Inc., Glycerol diacetate (50%) and glycerol triacetate ($\geq 99\%$) were purchased from Sigma Aldrich Co. Ltd., Acetonitrile ($\geq 99.9\%$) and acetic acid glacial ($\geq 99.8\%$), sulfuric acid ($\geq 98\%$), hydrochloric acid (37%) and glycerol ($\geq 99.5\%$) were obtained from Quality Reagent Chemical Co Ltd. Solvents were obtained from commercial sources.

3.2.2 Synthesis of s-GO catalyst

GO nanosheets (2.0 mg/mL) were synthesized via a modified Tour's method as previously mentioned. The GO suspension was dried in an oven at 60 °C for 24 h to obtain GO powder. GO powder (0.5 g) was transferred to a 250 mL three neck round bottom flask. Subsequently, 25 mL of concentrated H₂SO₄ (98%) was added to the flask following by sonication for 30 min. The mixture was heated to 85 °C and continuously stirred for 6 h. After completion, 400 mL of distilled water was added for dilution. The mixture was cooled down to room temperature and transferred to a 600 mL beaker. After that, the mixture was washed using distilled water and HCl by centrifugation several times. The solid products were collected and dried at 60 °C for 24 h to obtain the final s-GO catalyst.

3.2.3 Catalyst characterization

The surface morphology of the catalyst was observed by scanning electron microscopy (SEM; MIRA3, Tescan). In addition, the elemental composition on the catalyst surface was studied by energy dispersive X-ray spectroscopy (EDS). The structure of s-GO catalyst was analyzed by X-ray diffraction. Fourier transform infrared (FTIR) spectroscopy was employed to examine the presence of oxygen functionalized and sulfonated groups in the catalyst. The specific surface area of catalysts was determined by N₂-physisorption using the Brunauer-Emmett-Teller (BET) method. Ammonia temperature-programmed desorption (NH₃-TPD) was used to measure the total acid site concentration of catalysts by analyzing the desorption of ammonia with varying temperature.

3.2.4 Catalytic performance measurement

Esterification of glycerol with acetic acid was carried out in a 100 mL stainless-steel autoclave reactor. Prior to reaction, glycerol (9.21 g) and acetic acid (36.03 g) were preheated separately to the desired temperature then were mixed in an autoclave. Subsequently, the catalyst (5 wt.% relative to glycerol mass) was carefully loaded to the mixture to initiate the esterification process, followed by heating 120 °C with 900 rpm of stirring. After 2 h, the reaction mixture was collected and centrifuged to separate the catalyst for further use.

The recyclability of s-GO catalyst was evaluated in glycerol esterification with acetic acid under the optimized conditions. After reaction, the catalyst was recovered by centrifugation and washing thoroughly with ethanol and DI water. Subsequently, the catalyst was dried at 80 °C overnight and reused in the next cycle.

3.2.5 Product analysis

The reaction products were analyzed and quantified by high-performance liquid chromatography (HPLC) utilizing a gradient method and multiple columns. For product selectivity analysis, the reaction mixture (100 µL) was dissolved in 5 mL of water/ACN/DCM (40:59.6:0.4), and the prepared solution was injected into HPLC (Agilent 1260 Infinity II), using an Agilent HC-C18 reverse phase column (5 µm × 4.6 mm. I.D. × 250 mm length). For glycerol conversion analysis, the reaction mixture (100 µL) was dissolved in 5 mL of DI water, and the prepared solution was injected into HPLC with a Coregel 87H3 normal phase column (7.8 mm. I.D. × 300 mm length). The glycerol conversion and product selectivity were determined using the following equations.

$$X_G (\%) = \frac{C_{gly,0} - C_{gly}}{C_{gly,0}} \times 100 \quad (2)$$

$$S_{MAG} (\%) = \frac{C_{MAG}}{C_{MAG+DAG+TAG}} \times 100 \quad (3)$$

$$S_{DAG} (\%) = \frac{C_{DAG}}{C_{MAG+DAG+TAG}} \times 100 \quad (4)$$

$$S_{TAG} (\%) = \frac{C_{TAG}}{C_{MAG+DAG+TAG}} \times 100 \quad (5)$$

After reaction completion, the recyclability of s-GO catalyst was examined. The catalyst was recovered by centrifugation, followed by washing with ethanol and distilled water several times. Finally, the catalyst was dried in an oven at 60 °C overnight for the use of next reaction cycles.

CHAPTER 4

RESULTS AND DISCUSSION

The results and discussion of the two parts including; (1) Electrochemical hydrogenation using GO-based membrane reactor and (2) Catalysis of glycerol acetylation, were presented in this chapter. In the first part, the characteristics and electrochemical performance of the prepared Ce_Im_GO membrane have been discussed. The performance of electrochemical hydrogenation of nitro and carbonyl compounds using a GO-based membrane reactor has been demonstrated. Consequently, the properties and catalytic activities of s-GO catalysts for glycerol esterification were presented in the second part of this chapter. The results and discussion of the following are described below:

4.1 Electrochemical hydrogenation in a GO-based PEM reactor

4.1.1 Structural analysis of Ce_Im_GO membrane

XRD characterization was conducted to measure the influence of intercalated molecules on the layered structure of GO (Figure 10). GO synthesized via modified Tour's method showed a single diffraction peak (2θ) at 9.01° , with an interlayer spacing (d) of 0.98 nm, which is typical for GO indicated the successful GO synthesis. The increased interlayer spacing compared to the expanded graphite precursor with 0.339 nm at 26.24° and 54.37° resulted from the introduction of oxygen functional groups along the surface and edge of GO layers. Furthermore, the introduction of cerium ions and imidazole into the GO exhibited a shifted peak position to the lower angles ($2\theta = 7^\circ$) leading to d -spacing of 1.24 nm. This result suggested that the intercalated molecules occupied the GO interlayer that further enlarge the interlayer spacing.

The surface functionalities of GO membranes were analyzed by FTIR spectroscopy, as displayed in Figure 11. For pristine GO, a characteristic broad band of O–H stretching was presented between 3000 and 3600 cm^{-1} corresponding to O–H stretching, while other absorption bands, including C=O stretching of carbonyl and carboxylic acid groups, C=C skeletal vibration of the aromatic domains, C–OH

stretching, and C–O–C stretching of epoxy groups, were observed at approximately 1725 cm^{-1} , 1670 cm^{-1} , 1250 cm^{-1} , and 1045 cm^{-1} , respectively. These features confirm the presence of abundant oxygen-containing functional groups on the GO surface. After imidazole functionalization, notable spectral changes were observed, indicating successful incorporation of the imidazole moieties. The broad O–H stretching band around $3200\text{--}3400\text{ cm}^{-1}$ became more intense and slightly shifted, which can be attributed to overlapping N–H stretching vibrations from the imidazole ring and enhanced hydrogen bonding interactions. The C=O band at 1720 cm^{-1} decreased in intensity, suggesting partial reduction of GO and possible chemical interaction between the carboxylic groups of GO and the imidazole molecules. A new absorption band appeared around $1250\text{--}1350\text{ cm}^{-1}$, assigned to the C–N stretching vibration, confirming the presence of nitrogen-containing imidazole groups. Additionally, a weak band around $1550\text{--}1600\text{ cm}^{-1}$ was attributed to N–H bending or C=N stretching vibrations from the imidazole ring.

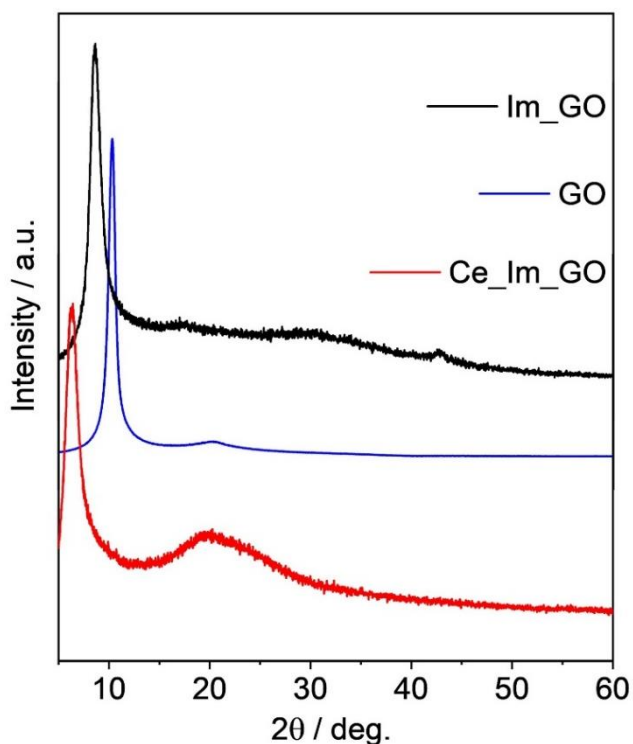


Figure 10 XRD patterns of GO, Im_GO, and Ce_Im_GO, displaying the shifted characteristics peak of GO.

To further investigate the surface elemental composition and chemical environment of the modified membrane, XPS analysis was performed. The survey spectrum of the Ce_Im_GO membrane depicts prominent peaks corresponding to carbon (C 1s) and oxygen (O 1s), confirming the presence of oxygenated functional groups (Figure 12). In addition, nitrogen (N 1s) and cerium (Ce 3d) peaks were detected. This result confirmed the functionalization of nitrogen-containing groups and cerium ions into the GO matrices.

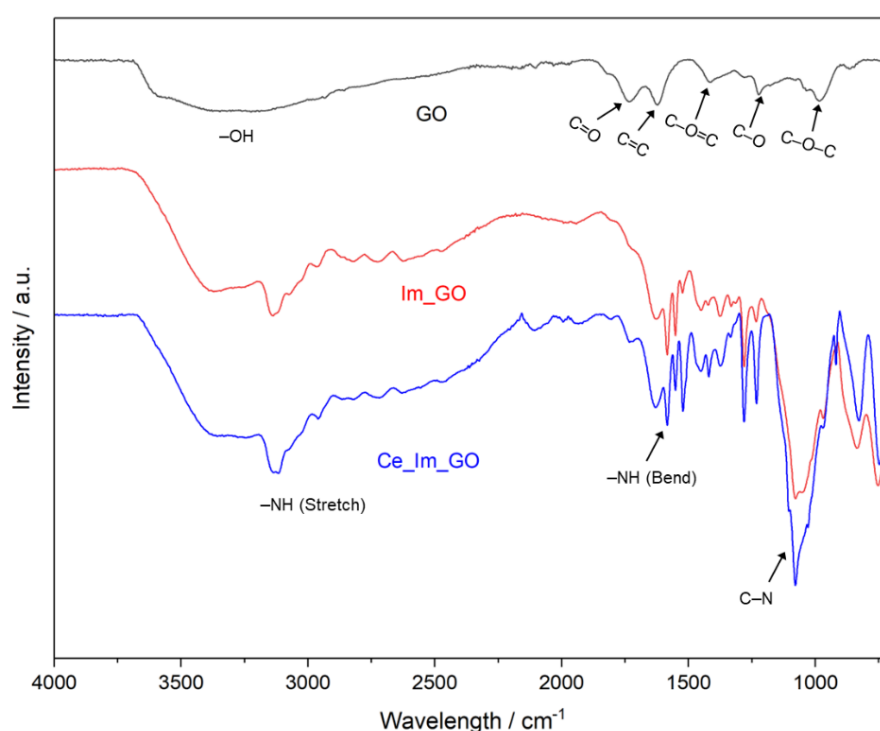


Figure 11 FTIR spectra of pristine GO, Im_GO, and Ce_Im_GO

The high-resolution C 1s spectrum could be deconvoluted into the following components: π -conjugated sp^2 -carbon C=C, sp^3 -carbon C-C, and C-H (~ 284.5 eV); C-OH (~ 285.3 eV); epoxide C-O-C (~ 286.6 eV); carbonyl C=O (~ 287.5 eV); and carboxyl O-C=O (~ 288.3 eV). Similarly, the N 1s spectrum of the modified GO membrane exhibited a protonated or coordinated nitrogen (~ 400.7 eV). These signals are characteristic of imidazole rings and further verify the successful incorporation of nitrogen species onto the GO surface. Upon the incorporation of

cerium ions, the mixed-valence cerium species, Ce^{3+} and Ce^{4+} , in the membrane was observed. Figure 14b shows the sharp peaks at ~ 885.7 and ~ 903.9 eV, which were ascribed to the Ce^{4+} oxidation state, significantly decreased. The results showed that Ce^{4+} ions were reduced to Ce^{3+} by coupling with GO nanosheets (Hamidah et al., 2021).

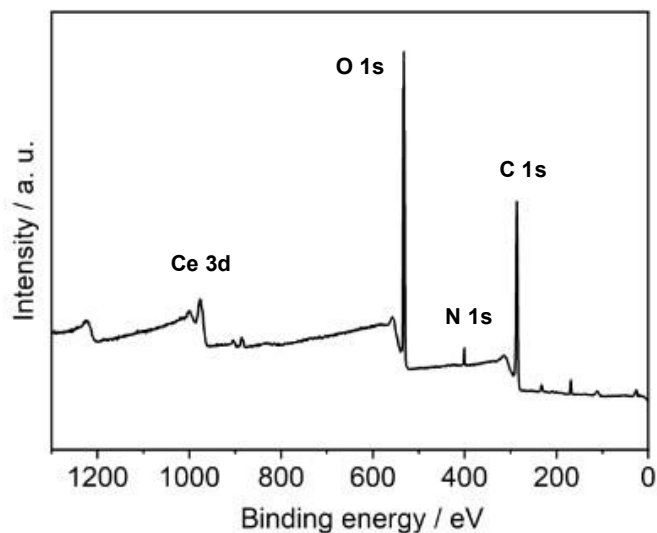


Figure 12 The XPS survey spectra of the Ce_Im_GO membrane.

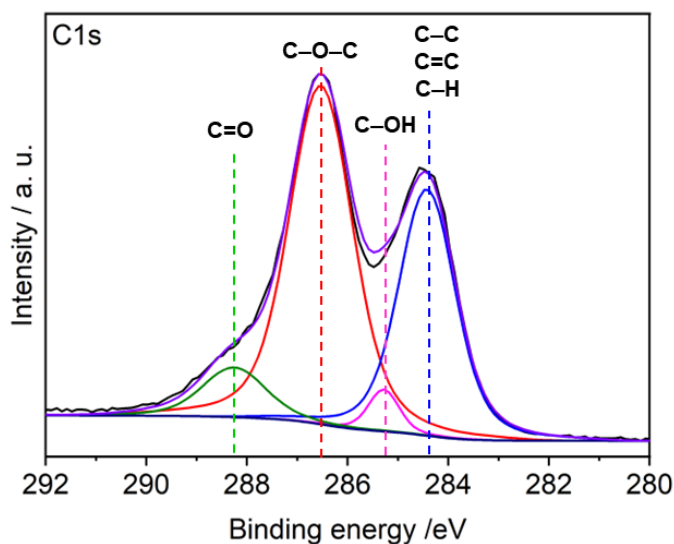


Figure 13 The high-resolution C 1s spectrum of the Ce_Im_GO membrane.

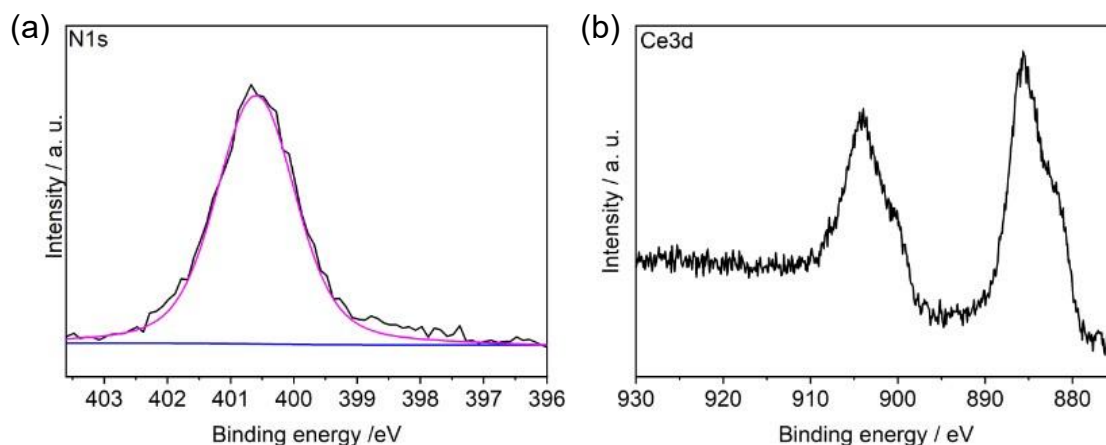


Figure 14 High-resolution (a) N 1s and (b) Ce 3d spectrums of the Ce_Im_GO membrane.

4.1.2 Morphological properties of Ce_Im_GO membrane

The morphology and structure of GO nanosheets synthesized by the Tours method was examined by SEM analysis. The cross-sectional SEM images of the membrane showed that GO nanosheets were uniformly stacked together, forming multi-layered GO membranes (Figure 15). Interestingly, the wrinkled structure of GO nanolayers was also observed from the SEM micrographs, indicating that defects and pores were formed on the GO nanosheets. This is attributed to the chemical oxidation of acids and exfoliation during the GO preparation process. In addition, energy dispersive analysis displayed the elemental distribution in the membranes, as shown in Figure 16. The functionalized nitrogen and cerium particles were clearly observed in EDS mappings, suggesting the success of the consistent deposition of imidazole and cerium ions on the stacked GO nanosheets.

4.1.3 Membrane stability in DI water

The stability of the modified membrane in distilled water was investigated by visual inspection. Figure 17 shows the membrane stability measurement by immersing the Ce_Im_GO membrane in distilled water for over 30 days. For pristine GO membrane, the disintegration of the membrane occurred after 30 min and was nearly complete after 9 days. The result suggested that negatively charged-GO nanosheets are highly hydrophilic, which was caused by the deprotonation of carboxyl

groups on the edges of GO structures. In contrast, the Ce_Im_GO membrane exhibits a significant improvement in structural stability. After 30 days, the membrane was still in perfect condition, which was attributed to the incorporation of cerium ions, causing the carboxylate formation between cerium ions and carboxyl groups on the edge of GO nanosheets. Importantly, this 3D cross-linking coordination effectively suppressed the disintegration of GO nanosheets in distilled water, improving the membrane stability.

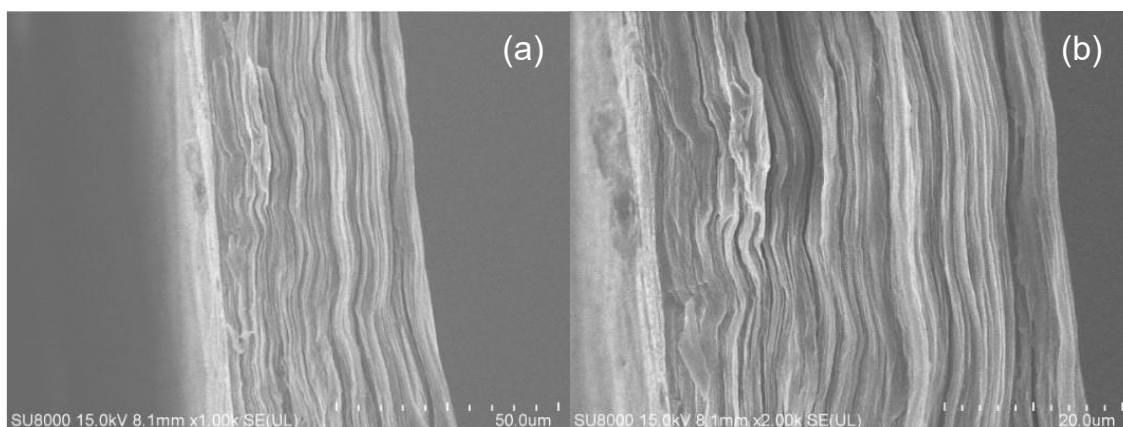


Figure 15 Cross-sectional SEM micrographs of the Ce_Im_GO membrane at amplitude of (a) 50 μm and (b) 20 μm .

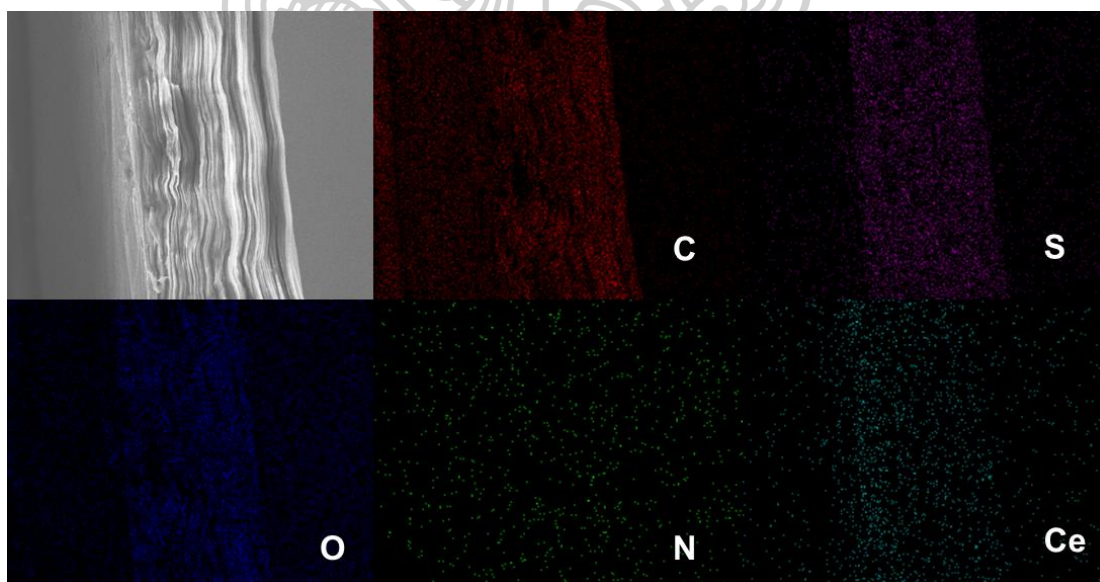


Figure 16 EDS mappings of the Ce_Im_GO membrane showing the deposition of incorporated species.



Figure 17 Stability in water of the cerium-modified Im_GO membrane for 30 days.

4.1.4 Electrochemical analysis of Ce_Im_GO membrane

The proton conductivity of the GO membranes was investigated by electron impedance spectroscopy (EIS). Figure 18 displays the Nyquist plots of pristine GO and modified membranes in synthetic air under 80% relative humidity at room temperature. The pristine GO membrane exhibited clear capacity semicircles in the lower frequency ranges.

To evaluate the proton transport behavior, concentration-cell measurements were employed. The resulting open-circuit potential (*EMF*) between the electrodes was measured, and the proton transfer number (*t*) was calculated using the following Nernst equation:

$$EMF = \frac{tRT}{nF} \ln \left(\frac{p'H_2}{p''H_2} \right) \quad (6)$$

where, *EMF* represents the electromotive force generated across the membrane, *t* is the proton transport number, *R* is the universal gas constant, *T* is the absolute temperature, *F* is Faraday's constant, *n* is the number of electrons transferred (*n* = 2 for the equilibrium $2H^+ + 2e^- \rightleftharpoons H_2$), and ($p'H_2 / p''H_2$) denote the partial pressures of hydrogen on each side of the membrane. The time-dependent *EMF* response of the Im_GO and Ce_Im_GO membrane at room temperature demonstrated high sensitivity to variations

in hydrogen partial pressure, as shown in Figure 19 and 20. A linear relationship between EMF and logarithmic ratio of H_2 concentrations ($\ln(p'H_2 / p''H_2)$) was observed with a slope of 28.2 mV/decade. This value is nearly close to the value of the theoretical Nernst slope (29.5 mV/decade) for a two-electron transfer process ($n = 2$), suggesting that the proton-coupled electron transfer occurred under equilibrium conditions.

Furthermore, the proton transport number of the Im_GO and Ce_Im_GO membranes were calculated using equation (6). The Im_GO membrane exhibited t of 0.540, indicating partial proton selectivity with some ionic crossover in the modified membrane that without cerium ions. In contrast, the Ce_Im_GO membrane achieved a t of 0.956, suggesting a highly selective proton conduction, which was attributed to the introduced cerium ions (Figure 20). Interestingly, a slight deviation at higher H_2 concentration suggests minimal electronic conductivity, however, the Ce-modified membrane exhibits as a dominant proton carrier at room temperature.

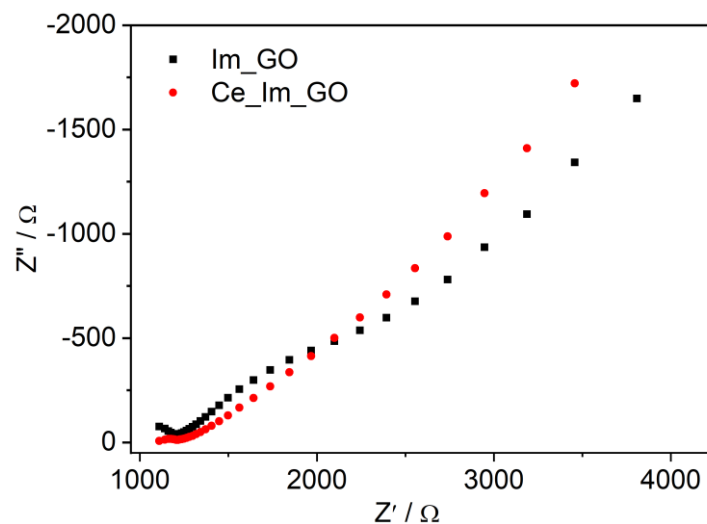


Figure 18 Nyquist plot of the Im_GO and Ce_Im_GO membranes under humidified conditions at room temperature.

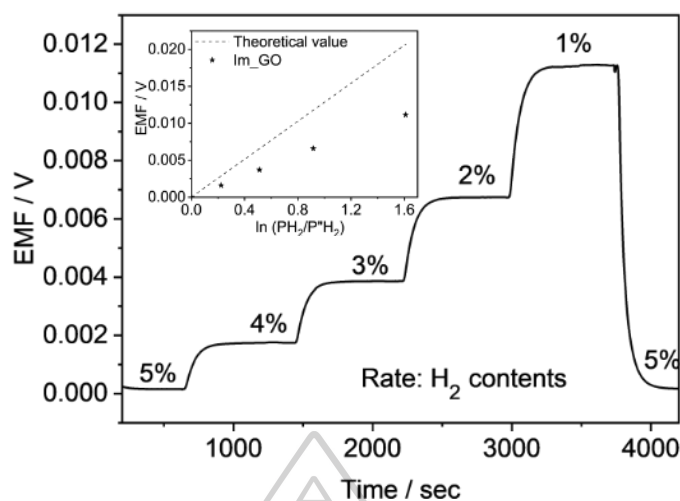


Figure 19 The EMF transient in response to hydrogen for Im_GO membrane. The inset shows the dependence of EMF on hydrogen concentration in Ar at room temperature.

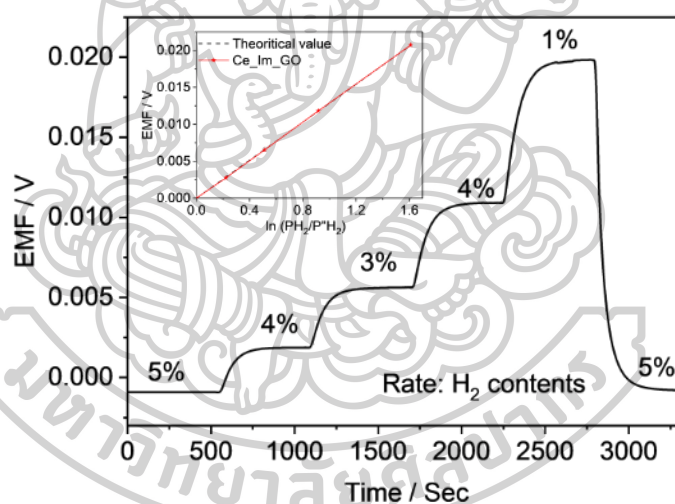


Figure 20 The EMF transient in response to hydrogen for Ce_Im_GO membrane. The inset shows the dependence of EMF on hydrogen concentration in Ar at room temperature.

4.1.5 Selective hydrogenation of nitro compounds

The performance of the dual functionalized GO membranes was evaluated in the electrocatalytic hydrogenation of nitrobenzene to aniline, where the modified membrane was served as the proton-conducting membrane in a PEM reactor. Hydrogenation experiments were carried out under ambient pressure and temperature for 24 h at applied current densities of 50 and 100 mA·cm⁻². Figure 21 displays the

dependence of aniline yield on reaction time at different applied current densities under atmospheric conditions. After 24 h, a maximum conversion of 90% of nitrobenzene to aniline was achieved when applying current densities $\geq 100 \text{ mA}\cdot\text{cm}^{-2}$. As expected, the overall hydrogenation performance increased with both current density and reaction time.

To confirm that the reduction of nitrobenzene originated from electrochemically generated protons rather than spontaneous thermal hydrogenation or simple membrane contact, a control experiment was performed without supplying any external current ($0 \text{ mA}\cdot\text{cm}^{-2}$). Under these conditions, no significant conversion of nitrobenzene was observed after 24 h. This result clearly indicates that the hydrogenation is driven by proton transport through the GO-based membrane under an applied electric field, confirming the essential role of the membrane in facilitating electrochemical hydrogenation.

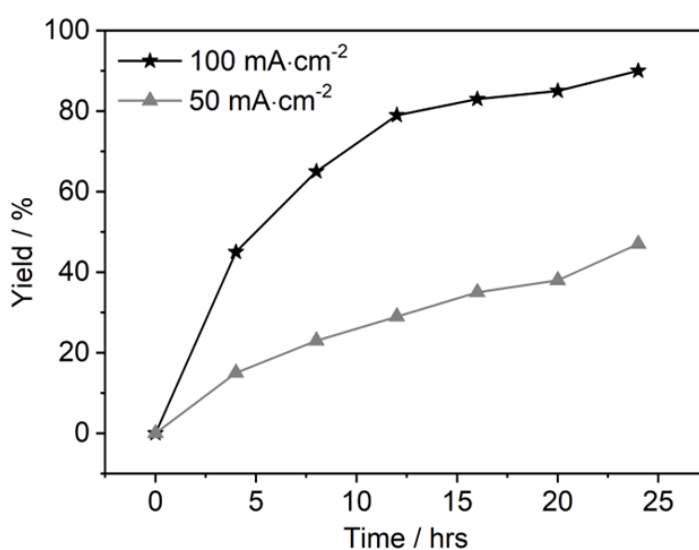


Figure 21 Dependence of aniline yield and reaction time at different applied current densities.

Based on the optimized conditions, the hydrogenation of nitrobenzene derivatives with various substituted functional groups was subsequently investigated (entries 1-6, Table 3). Nitrobenzene derivatives with electron-donating substituents, such as 3-nitrotoluene (entry 1), *p*-nitrotoluene (entry 2), and 4-nitroanisole (entry 3),

exhibited high hydrogenation yields of 85%, 89%, and 87%, respectively. Electron-donating groups increase the electron density on the aromatic ring and reduce the electron-withdrawing character of $-\text{NO}_2$ group, thereby stabilizing intermediate species formed during protonation and facilitate stepwise reduction pathway. These results are consistent with classical substituent effects observed in hydrogenation chemistry (Ref). Interestingly, the position of the substituents also played a noticeable role. The *para*-methyl derivative (entry 1, 89%) exhibited a slightly higher yield than the *meta*-position (entry 2, 85%), suggesting that the *para*-position may produce less steric effect interference near the nitro group and impose fewer resonance interactions than *meta* substitution. This phenomena thereby enables more favorable kinetics for proton-coupled electron transfer. Meanwhile, *para*-methoxy (entry 3, 87%) provided similar reactivity but is electronically distinct due to strong mesomeric donation, which stabilizes the intermediate nitroso/hydroxylamine species.

A nitrobenzene containing electron-neutral substituent, allyl-nitrobenzene (entry 4) also produced the corresponding aniline in 79% yield, demonstrating that substituents without strong inductive or resonance effects still undergo efficient hydrogenation in the PEM reactor. Surprisingly, the yields of derivatives containing electron-withdrawing groups, such as 3-chloro-nitrobenzene (entry 5, 90%) and *p*-bromo-nitrobenzene (entry 6, 84%), were similar or even higher than the derivatives containing electron-donating groups. This behavior contrasts with classical homogeneous hydrogenation trends where electron-withdrawing substituents often decrease the hydrogenation efficiency, as they lower electron density on the aromatic ring and slow reaction kinetics. This observation may be attributed to the enhanced proton availability and controlled electron transfer in the PEM reactor, which compensates for electronic deactivation.

Overall, these results demonstrate that the electronic effects of substituents play an essential role in determining hydrogenation efficiency in the GO-based PEM reactor. Electron-donating substituents facilitate proton-assisted hydrogenation pathways for the reduction of $-\text{NO}_2$ to $-\text{NH}_2$. Importantly, the no-current control verifies that the GO-based membrane reactor operates through electrochemical proton transport, not spontaneous chemical reduction. The system exhibits remarkable

chemoselectivity, functional-group tolerance, and stability, making it highly suitable for selective nitro-group hydrogenation under mild conditions.

Table 3 List of electrochemical hydrogenations of substituted nitro compounds using the GO-based PEM reactor.

Entry	Reactant	Product	Yield (%) ^b	Selectivity (%)
1			85	>99
2			89	>99
3			87	>99
4			79	>99
5			90	>99
6			84	>99

4.1.6 Selective hydrogenation of carbonyl compounds

To further evaluate the performance of the GO-based PEM reactor, the electrocatalytic hydrogenation of various aromatic ketone compounds was investigated (entries 7-10, Table 4). These substrates serve as important intermediates in chemical synthesis and pharmaceutical manufacturing. All reactions were performed under the same optimized conditions as previously described. Acetophenone (entry 7) was effectively hydrogenated to phenylethanol in 83% yield with high purity, confirming the capability of the PEM reactor to reduce aromatic carbonyl groups. In contrast to nitro groups, substituted aromatic ketones exhibited moderate to good yields of the corresponding alcohols. Carbonyl compounds with electron-donating substituents, such

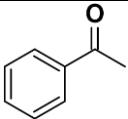
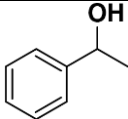
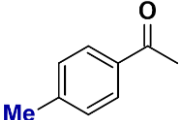
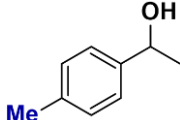
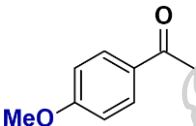
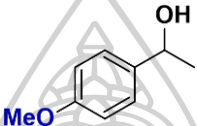
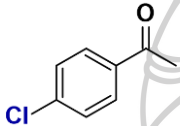
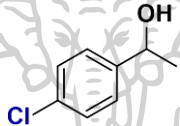
as *p*-methylacetophenone (entry 8) and 4-methoxyacetophenone (entry 9), showed a good hydrogenation yield of 82% and 79%, whereas the electron-withdrawing containing derivative, 4-chloroacetophenone (entry 10), achieved 87% yield. These variations highlight the influence and interactions between electronic and positional effects in the hydrogenation of aromatic ketones.

From an electronic perspective, electron-withdrawing substituents (e.g., –Cl) make the carbonyl carbon more electrophilic, facilitating the nucleophilic attack by electrochemically generated hydrides/protons and lowering the activation barrier for hydrogenation. In contrast, the methyl and methoxy groups donate electron density to the carbonyl group via resonance, stabilizing the C=O bond and reducing its susceptibility to reduction.

In comparison with nitroarene hydrogenation, the reduction of aromatic ketones resulted in slightly lower yields. This difference reflects the intrinsic difficulty associated with hydrogenolysis of the C=O group, which is more resonance-stabilized and requires a higher activation barrier for protonation. Nevertheless, the PEM reactor's ability to hydrogenate ketones under ambient conditions demonstrates the efficiency of proton transport and the catalytic competency of the system. Notably, all reactions proceeded with excellent chemoselectivity, with no detectable benzene-ring hydrogenation or formation of side-products. This high selectivity confirms that the proton-conductive environment created by the GO membrane allows controlled and targeted reduction of the carbonyl group, offering favorable pathways for fine-chemical synthesis and potential applications in hydrogen-relevant transformations.

Overall, the electrochemical hydrogenation of both aromatic nitro compounds and ketone derivatives exhibited excellent selectivity, with no detectable side reactions or impurities other than trace formation of hydrogenated benzene-ring by-products. These results demonstrate that the GO-based PEM reactor provides an efficient and selective platform for electrocatalytically converting a broad spectrum of aromatic organic compounds under mild conditions. The stable performance and high chemoselectivity of the system highlight its potential for further application in liquid-phase hydrogenation processes and its relevance to H₂ storage and conversion technologies.

Table 4 List of electrochemical hydrogenations of substituted carbonyl compounds using the GO-based PEM reactor.

Entry	Reactant	Product	Yield (%) ^b	Selectivity (%)
7			83	>99
8			82	>99
9			79	>99
10			87	>99

4.2 Catalysis of glycerol acetylation

4.2.1 Structural analysis of s-GO catalyst

The crystalline structure of the sulfonated GO was investigated by XRD, with the pattern shown in Figure 22. The XRD pattern of the sulfonated graphene oxide displays a distinct diffraction peak at $2\theta \approx 10.5^\circ$, which corresponds to the (001) reflection plane of graphene oxide. This peak is slightly shifted from the pristine GO, which indicates an increased interlayer spacing due to the introduction of oxygenated and sulfonic functional groups between the graphene sheets. In addition to the main peak, the broad and low-intensity hump is observed in the region of $20\text{--}30^\circ$, suggesting a partial loss of long-range crystalline order and the formation of a more amorphous carbon structure after sulfonation. This feature is characteristic of disordered GO networks and indicates the successful introduction of acidic functionalities, which disrupt the graphitic stacking order and enhance catalytic surface accessibility.

FTIR spectroscopy provides further evidence for the successful sulfonation of GO (Figure 4-13b). Several absorption bands corresponding to oxygen-containing functional groups were confirmed in the FTIR spectra of s-GO, as previously described.

Importantly, new absorption peaks emerge at approximately 1180 and 1040 cm^{-1} , corresponding to the asymmetric and symmetric stretching vibrations of the S=O bonds in sulfonic acid ($-\text{SO}_3\text{H}$) groups. The presence of these characteristic bands provides clear evidence that sulfonic groups have been successfully grafted onto the GO surface.

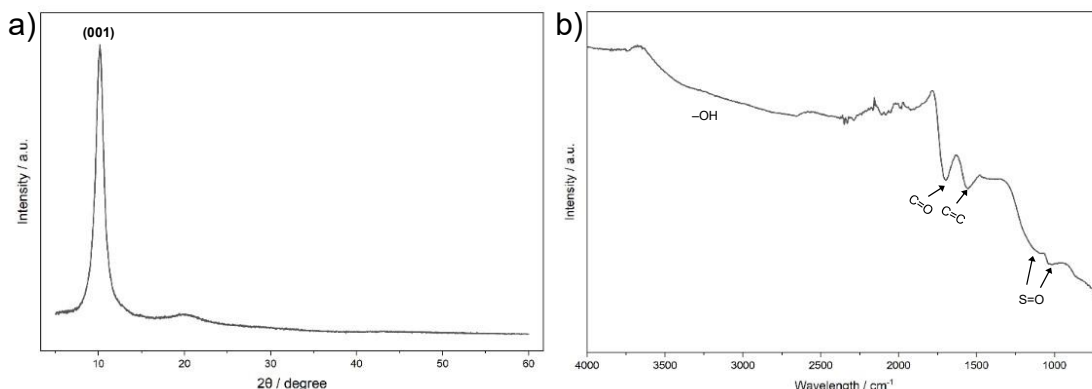


Figure 22 (a) XRD pattern and (b) FTIR spectra of the synthesized s-GO catalyst.

4.2.2 Morphological analysis of s-GO catalyst

The morphology of the synthesized s-GO catalyst was examined using SEM, as shown in Figure 23. The SEM images reveal the crumpled flake-like structure of the catalyst, which is the characteristic of exfoliated GO derivatives. The wrinkled and irregular nature is consistent with the oxidation and subsequent sulfonation steps, which disrupt the π - π stacking between layers and promote partial exfoliation. The average lateral size of the visible flakes ranges from 10-100 μm , indicating that the sulfonation process did not significantly fragment the GO sheets, which is consistent with previous reports for chemically functionalized GO.

Elemental composition was further analyzed by EDS as represented in Figure 24. Prominent peaks corresponding to C, O, and S were observed, confirming the successful introduction of sulfur-containing groups onto the GO framework. Quantitatively, the s-GO sample contains 34.08 wt.% C, 41.86 wt.% O, and 9.36 wt.% S (Table 6). The presence of sulfur content at nearly 5 atomic % suggests that, in addition to covalently attached $-\text{SO}_3\text{H}$ groups, a portion of the detected sulfur may originate from physisorbed or intercalated sulfate species that remain associated with

the highly oxygenated and hydrophilic GO surface. Such elevated sulfur levels can arise from strong adsorption of concentrated H_2SO_4 onto oxygen-rich sites, partial trapping of sulfate ions with folded or restacked GO layers, and the fact that steric hindrance limits covalent sulfonation but does not prevent the adsorption of smaller sulfate ions. The highly oxidized nature of the starting GO also provides abundant sites that facilitate both sulfonation and sulfate adsorption. The relatively high oxygen content reflects both the intrinsic oxygenated functionalities of GO produced via Tour's method and the possible presence of adsorbed sulfate species. Together, these oxygenated groups and sulfonic acid functionalities contribute to the overall acidity and hydrophilicity of the s-GO catalyst.

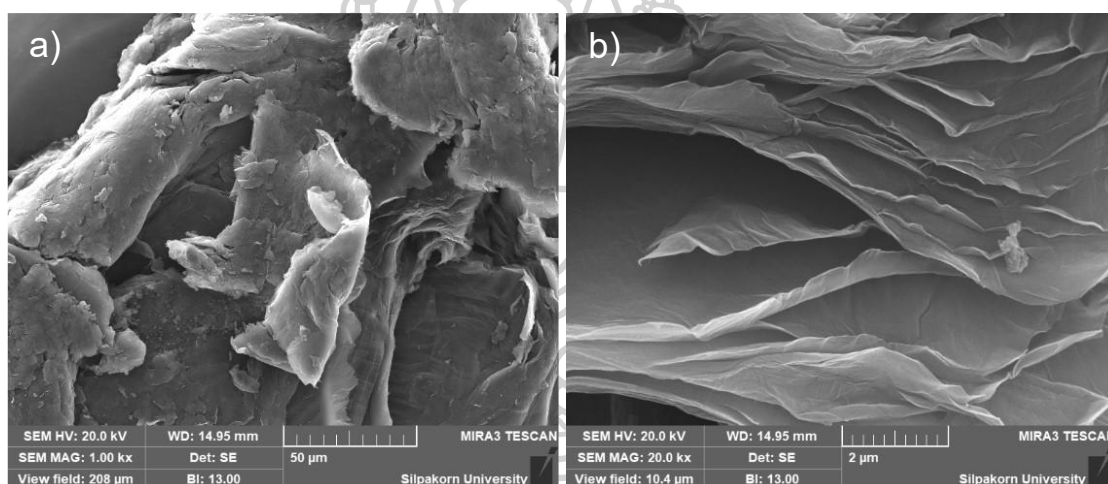


Figure 23 SEM images of the s-GO catalyst at magnifications of a) 50 μm and b) 2 μm .

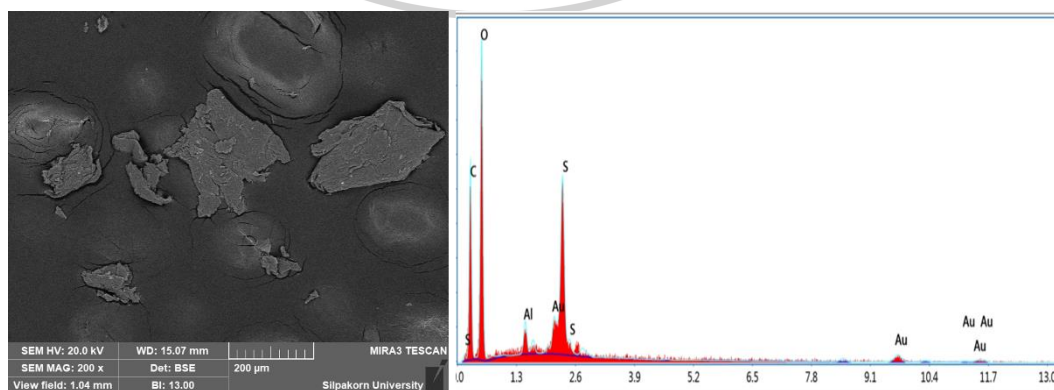


Figure 24 EDS elemental analysis of the s-GO catalyst displaying peaks corresponding to C, O, and S.

4.2.3 N₂-physisorption

The nitrogen adsorption-desorption isotherm and pore size distribution curve of the sulfonated GO are shown in Figure 25. The isotherm exhibits a nearly linear relationship between the adsorbed nitrogen volume (V_a) and the relative pressure (p/p_0), indicating that the adsorption process occurs primarily on the external surface of the GO layers and within interparticle voids, rather than through microporous adsorption. A weak hysteresis loop attributed to slit-like pores of the stacking lamellar sheets, was observed. The isotherm behavior suggests that GO functionalized with –SO₃H groups possesses a disordered layered morphology with limited mesoporosity.

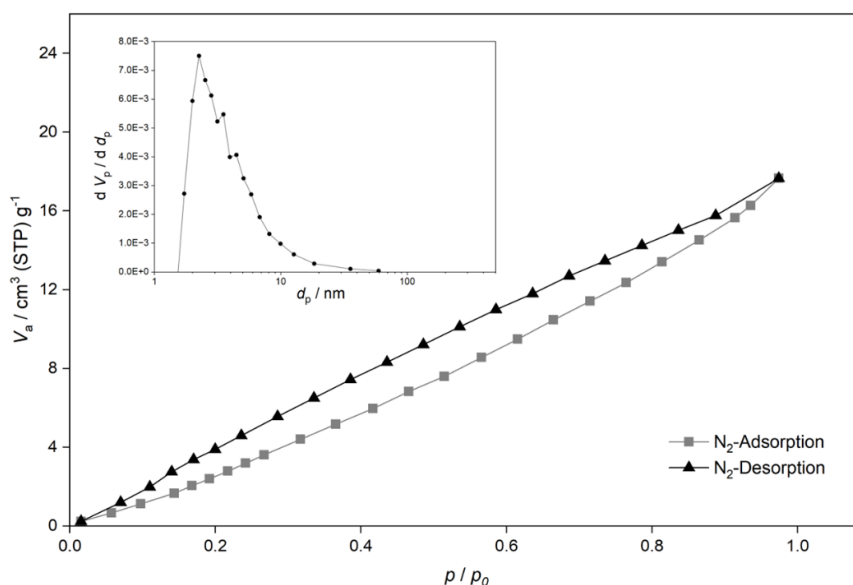


Figure 25 The adsorption/desorption isotherm plot of s-GO catalyst; the inset showing the BJH plot of the pore size distribution.

The BET surface area of the catalyst was calculated to be 37.97 m²/g. The relatively low surface area can be attributed to the introduction of –SO₃H groups, which partially block surface pores and promote agglomeration of the GO sheets during the sulfonation process. Meanwhile, the total pore volume of the catalyst is 0.04 cm³/g with the BJH average pore diameter of 5.09 nm. The results suggest the material predominantly contains mesoporous structures, facilitating the effective diffusion of reactant molecules and product desorption during catalytic reactions.

4.2.4 Catalytic performance on glycerol acetylation

The catalytic performances of GO and s-GO catalysts in glycerol acetylation are summarized in Table 5. Esterification reactions were carried out under optimized conditions obtained from previous literatures (glycerol-to-acetic acid molar ratio of 1:9, 120 °C, and 5 wt.% of catalyst loading). In the absence of a catalyst, glycerol conversion reached 61.8%, indicating that the esterification can proceed via a self-catalyzed mechanism under elevated temperature and with excess acetic acid. Nevertheless, only a moderate amount of monoacetin was formed, whereas diacetin and triacetin were nearly absent. This verifies that a solid acid catalyst is essential for facilitating the total esterification pathway from monoacetin to higher acetins. When pristine GO was employed, the conversion significantly increased to 98.6%, suggesting an enhancement of catalytic performance. This improvement is attributed to the presence of abundant oxygen-containing functional groups (e.g., –OH, –COOH, and C–O–C), which provide weak Brønsted and Lewis acidic sites capable of accelerating the esterification rate.

Table 5 Catalytic performance of GO, s-GO, and other solid acid catalysts in glycerol acetylation.

Catalyst	Conversion (%)	Selectivity (%)		
		Monoacetin	Diacetin	Triacetin
Blank	61.8			
GO	98.6	5.8	67.9	26.3
s-GO	99.8	1.2	69.5	29.3
ZSM-48 ^a	68.0	35.7	58.0	6.3
ZSM-5 ^a	76.3	30.8	62.2	7.0
H-mordenite ^a	75.0	35.3	58.3	6.4
WO ₃ /ZrO ₂ ^a	74.2	36.9	56.7	6.4
HPW/ZrO ₂ ^a	73.2	38.7	55.4	5.9

^a All other catalysts data was obtained from Zhou et al., 2013.

Although sulfonation was expected to significantly enhance catalytic performance, the glycerol acetylation results show that GO and s-GO show very similar overall activity, with both catalysts achieving almost complete glycerol conversion

(98.6% for GO and 99.8% for s-GO). This indicates that pristine GO already possesses sufficient acidic oxygenated groups to efficiently catalyze esterification under the applied reaction conditions. Therefore, the introduction of $-\text{SO}_3\text{H}$ groups does not substantially increase conversion under these mild conditions, where the reaction is largely kinetically favored.

Nevertheless, sulfonation does lead to a measurable yet modest improvement in product selectivity. The triacetin yield increased from 26.3% (GO) to 29.3% (s-GO), accompanied by slightly higher diacetin formation. This trend aligns with the expected role of $-\text{SO}_3\text{H}$ groups as strong Brønsted acid sites, which facilitate the consecutive esterification steps (monoacetin $\rightarrow$ diacetin $\rightarrow$ triacetin). The improvement is relatively small because the density of sulfonic groups introduced in this work is limited and the catalyst surface area is significantly reduced, likely due to pore blocking and sheet agglomeration during sulfonation. Both effects restrict the number of accessible acidic sites, which limits the magnitude of catalytic enhancement. These findings suggest that while sulfonation increases acidity, its catalytic benefit is partially offset by structural changes (reduced surface area, partial pore blockage). Therefore, future optimization should focus on increasing sulfonation efficiency without compromising the textural properties of the GO sheets, for example through milder sulfonation agents, post-sulfonation exfoliation, or interlayer spacing control.

For comparative purposes, previously reported solid-acid catalysts such as ZSM-5, ZSM-48, WO_3/ZrO_2 , and heteropolyacid-supported materials typically exhibit high glycerol conversion ($>90\%$) with triacetin selectivity in the range of 20–35%, depending on the reaction conditions (Table 5). These literature values demonstrate that the catalytic performances of GO and s-GO obtained in this study fall within the typical activity-selectivity window of established solid-acid catalysts, despite the much simpler, metal-free nature of GO-based materials. This contextual comparison further indicates that GO-based catalysts can serve as viable alternatives for glycerol acetylation in terms of both activity and selectivity.

The minimal difference in catalytic activity between GO and s-GO also indicates that, under the chosen reaction conditions (1:9 molar ratio, 120 °C, 5 wt.% catalyst), the system operates near the kinetic ceiling for glycerol acetylation. Both catalysts are sufficiently active to reach this upper limit within the reaction time,

meaning that further increases in acidity do not transform into proportionate increases in conversion. Thus, the effect of sulfonation is more evident in selectivity patterns rather than total conversion. This limitation should be recognized when evaluating acidity-activity relationships in highly effective carbon-based catalysts.

4.2.5 Recyclability of s-GO catalysts

The reusability of the sulfonated graphene oxide (s-GO) catalyst was evaluated through consecutive glycerol acetylation cycles to assess its stability and heterogeneity. The s-GO catalyst initially achieved a glycerol conversion of 99.8%, which only slightly decreased to 99.1% after the second run and 98.5% after the third run (Figure 26). A moderate decline in activity was observed after the fourth cycle, with conversion decreasing to approximately 87.8%. This gradual loss of activity can be primarily attributed to the partial hydrolysis or leaching of surface $\text{-SO}_3\text{H}$ groups, which slightly reduces the Brønsted acidity of the catalyst over successive cycles. Importantly, no significant structural degradation of the graphene framework was detected, suggesting that the catalyst retains its structural integrity and that deactivation is mainly chemical rather than physical.

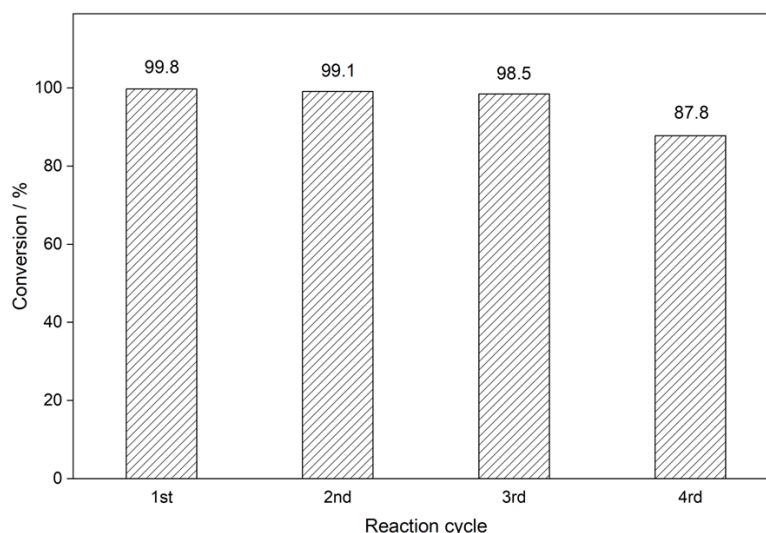


Figure 26 Dependence of glycerol conversion at different reaction cycles.

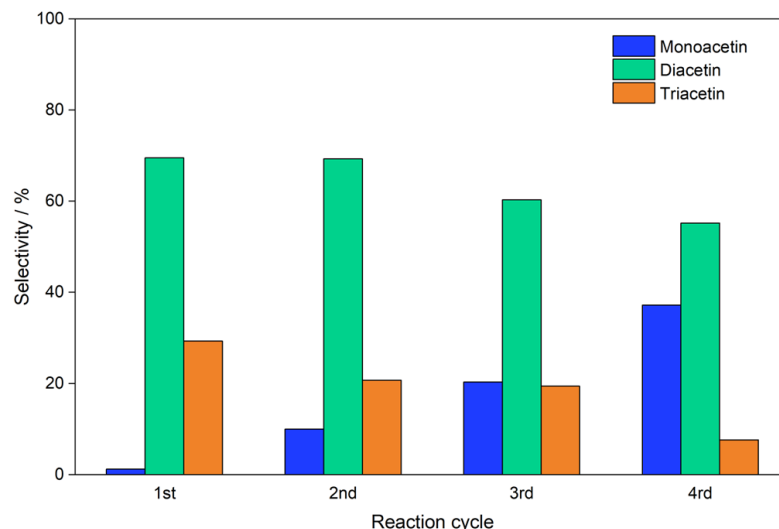


Figure 27 Dependence of product selectivities at different reaction cycles.

In addition, the relationship between the reaction cycles and the product selectivity toward mono-, di-, and triacetin was presented in Figure 27. It was observed that the selectivity to monoacetin increased with the number of reuse cycles, while the selectivities toward diacetin and triacetin slightly decreased. This shift in product distribution can be correlated with the reduction in the number and strength of acid sites, particularly the loss of $\text{-SO}_3\text{H}$ groups that are essential for promoting the consecutive esterification steps of monoacetin to triacetin.

Overall, these findings confirm that s-GO exhibits excellent short-term stability and reusability, maintaining nearly complete glycerol conversion through at least three consecutive reaction cycles. For extended use, however, regeneration treatments such as oxidative washing or mild calcination may be required to restore the density of active sulfonic groups and recover its initial catalytic performance. The stable catalytic behavior, coupled with its high conversion and selectivity, demonstrates the potential of s-GO as a durable and sustainable solid acid catalyst for glycerol valorization processes.

CHAPTER 5

CONCLUSIONS

5.1 Conclusion

This research explored the development of functionalized graphene oxide (GO) materials for two distinct applications: (i) proton-conducting membranes for electrochemical hydrogenation, and (ii) solid acid catalysts for glycerol acetylation. The results demonstrate that targeted chemical modification of GO can selectively enhance its physicochemical properties while maintaining its intrinsic advantages as a low-cost, metal-free material.

For the membrane study, imidazole and cerium ions were successfully introduced into the GO framework, as confirmed by XRD, FTIR, XPS, and SEM-EDS analyses. The functionalized CeIm-GO membrane exhibited improved proton conductivity (0.160 mS/cm) and excellent proton selectivity ($t = 0.96$), accompanied by enhanced mechanical stability in humid conditions. These improvements enabled efficient electrochemical hydrogenation of aromatic nitro compounds and ketones using a GO-based membrane reactor under mild operating conditions (ambient temperature and atmospheric pressure), demonstrating the potential of functionalized GO membranes as alternatives to conventional polymer electrolytes. Furthermore, this architecture offers promising potential for hydrogen-relevant technologies, particularly energy storage and conversion, demonstrating the broader versatility of GO-based systems in both catalytic and electrochemical domains.

For the catalytic study, sulfonated GO (s-GO) was synthesized and evaluated in glycerol acetylation. Although pristine GO already exhibited high catalytic activity due to its oxygen-containing functional groups, sulfonation introduced $-\text{SO}_3\text{H}$ groups that provided stronger Brønsted acidity. As a result, s-GO delivered slightly higher selectivity toward diacetin and triacetin compared to GO while maintaining nearly identical total conversion. The modest difference in performance reflects the strong inherent activity of GO under the reaction conditions and the reduced surface area caused by sulfonation. The recyclability evaluation confirmed the heterogeneous and reusable nature of the s-GO catalyst, which represents a promising, water-tolerant, and

environmentally friendly solid acid catalyst for glycerol valorization and other biomass-derived transformations.

Overall, this study demonstrates that graphene oxide is a highly versatile carbon-based material that can be applied for electrochemical and catalytic systems. Their tunable surface chemistry, strong acidity, and structural durability position GO-based materials as promising candidates for next-generation technologies in green energy conversion, biomass upgrading, and sustainable hydrogen utilization.

5.2 Recommendations

Based on the outcomes of this study, the following recommendations are proposed for future research and development of GO-based catalytic and electrochemical systems:

- 1) Further optimization of membrane thickness, ionic conductivity, and permeability should be performed to enhance proton transport efficiency and selectivity under real operating conditions. Such improvements would help increase the overall performance and stability of the GO-based membrane reactor for electrochemical hydrogenation processes.
- 2) Because s-GO and GO showed very similar catalytic activity under the studied conditions, indicating a possible kinetic ceiling, future work should focus on accurately quantifying acid-site density and strength. Techniques including acid-base titration, potentiometric titration, NH_3 -TPD, and pyridine-adsorbed FTIR can help distinguish contributions from Brønsted versus Lewis sites and clarify how sulfonation modifies the active functionalities.
- 3) The modest catalytic improvement from sulfonation suggests that structural effects, such as pore blockage and sheet restacking, counteracted the increase in acidity. Alternative sulfonation routes (e.g., chlorosulfonic acid, fuming sulfuric acid, diazonium sulfonation) should be investigated to increase accessible – SO_3H density without compromising textural properties..
- 4) As GO already achieves near-complete conversion under 120 °C and 1:9 molar ratio conditions, future studies should vary the key reaction parameters, including temperature, molar ratio, catalyst loading, and water-removal strategies, to determine conditions where acidity differences become more

influential. Lower-temperature or lower-acid conditions may reveal clearer performance distinctions between GO and s-GO. This systematical investigation is necessary to establish optimal conditions for maximum conversion and selectivity toward triacetin.

- 5) Detailed mechanistic and kinetic studies should be conducted to clarify the reaction pathways involved in glycerol acetylation over GO-based catalysts. Advanced *in situ* and *operando* characterization techniques such as FT-IR, Raman, and electrochemical spectroscopy could provide valuable insights into the active-site behavior and water adsorption mechanisms during catalysis.





APPENDIX A

HYDROGENATION REACTOR DESIGN

The design and configuration of a GO-based membrane reactor employed for electrochemical hydrogenation is displayed in Figure 28.

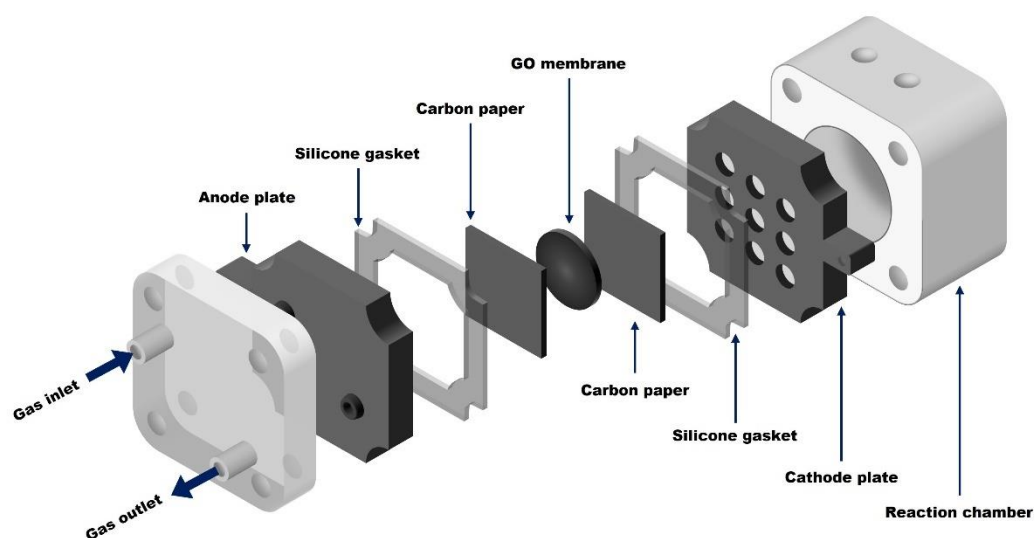


Figure 28 A schematic displaying a configuration of a GO-based PEM reactor.



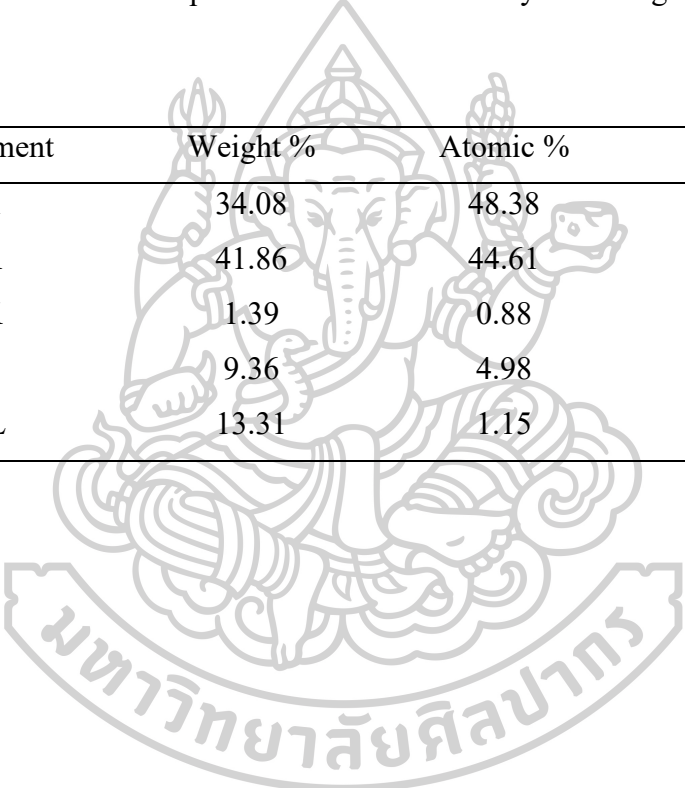
APPENDIX B

CATALYST CHARACTERIZATIONS

- **SEM-EDX**

The elemental analysis of the synthesized s-GO catalyst investigated by SEM-EDX technique is summarized in Table 6.

Table 6 The elemental composition of the s-GO catalyst investigated by SEM-EDX technique.



Element	Weight %	Atomic %	Net Int.
C K	34.08	48.38	353.93
O K	41.86	44.61	635.01
AlK	1.39	0.88	79.31
S K	9.36	4.98	523.99
AuL	13.31	1.15	40.39

- **BJH Analysis**

The detail of pore size distribution of the s-GO catalyst determined by BJH analysis is shown in Figure 29.

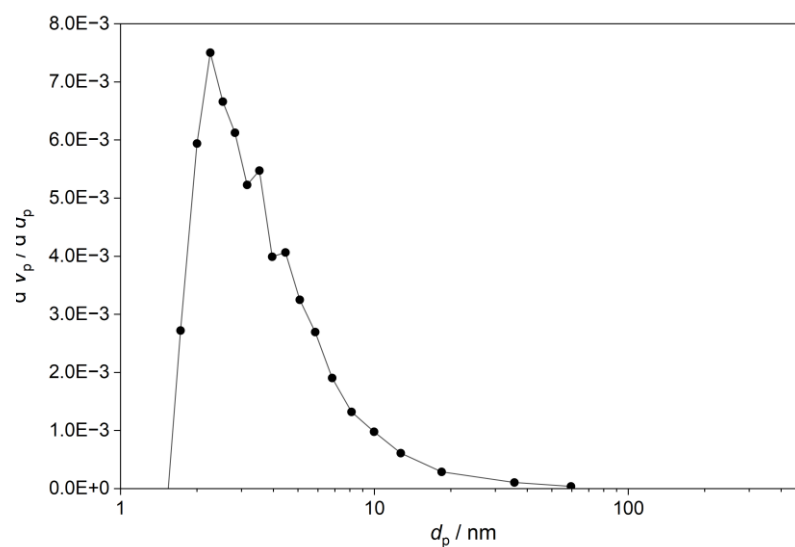
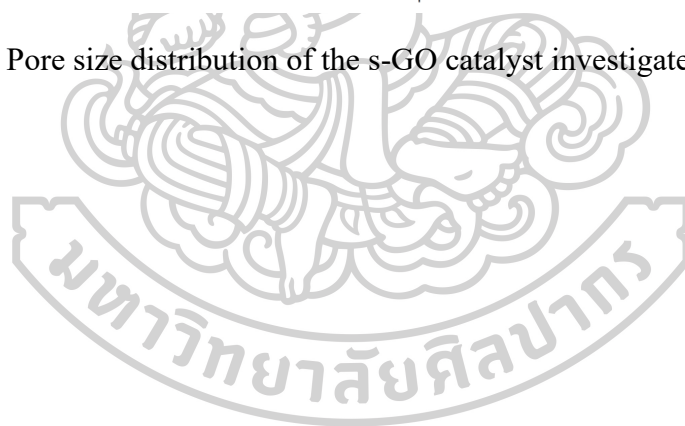


Figure 29 Pore size distribution of the s-GO catalyst investigated by BJH analysis.



APPENDIX C

PRODUCT CALCULATIONS

The catalytic performance on glycerol esterification, including conversion and selectivity, was evaluated by HPLC analysis, where the calibration curves are displayed below:

- **Calibration curve of glycerol**

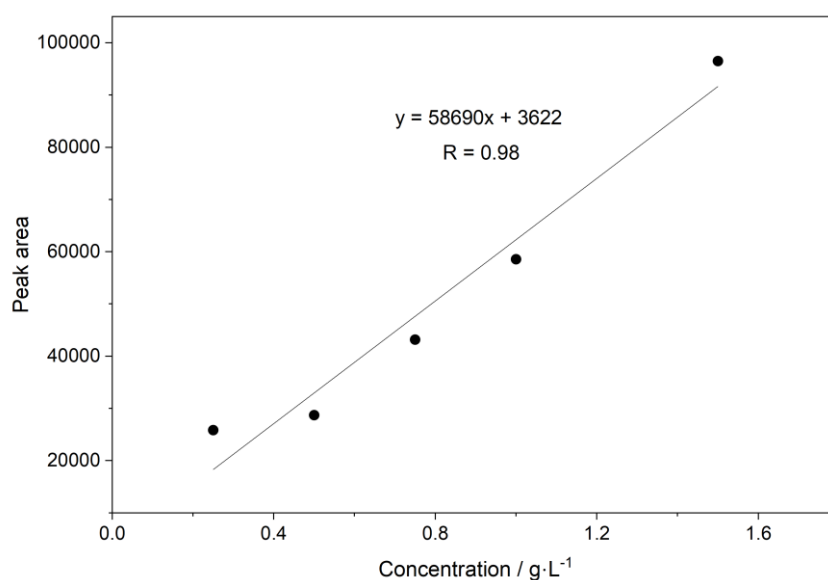


Figure 30 Calibration curve of glycerol.

- **Calibration curve of monoacetin**

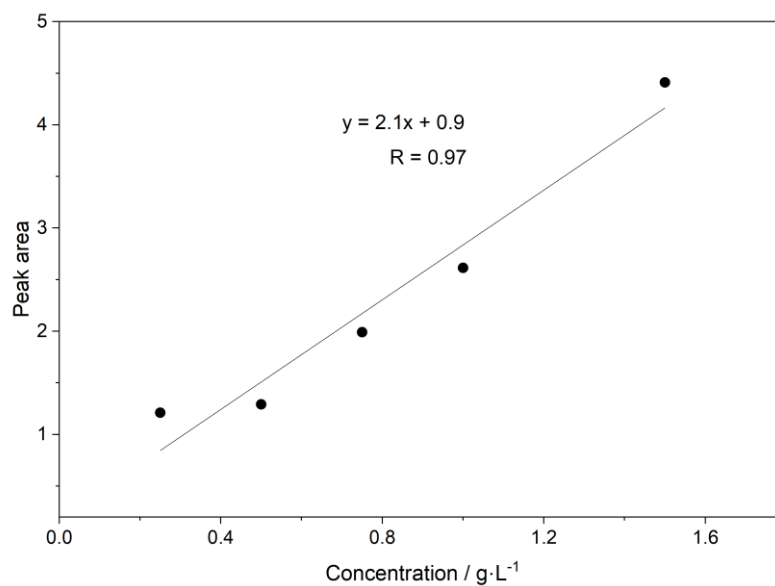


Figure 31 Calibration curve of monoacetin.

- **Calibration curve of diacetin**

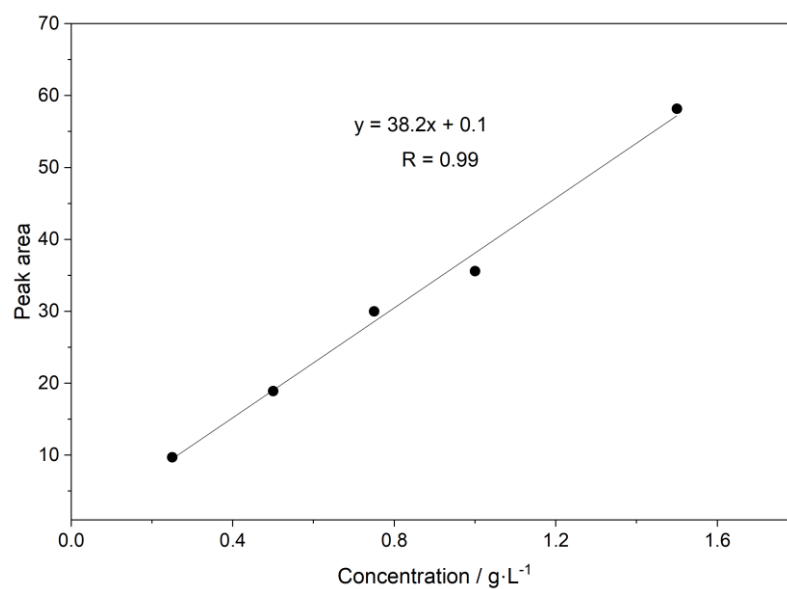


Figure 32 Calibration curve of diacetin.

- Calibration curve of triacetin

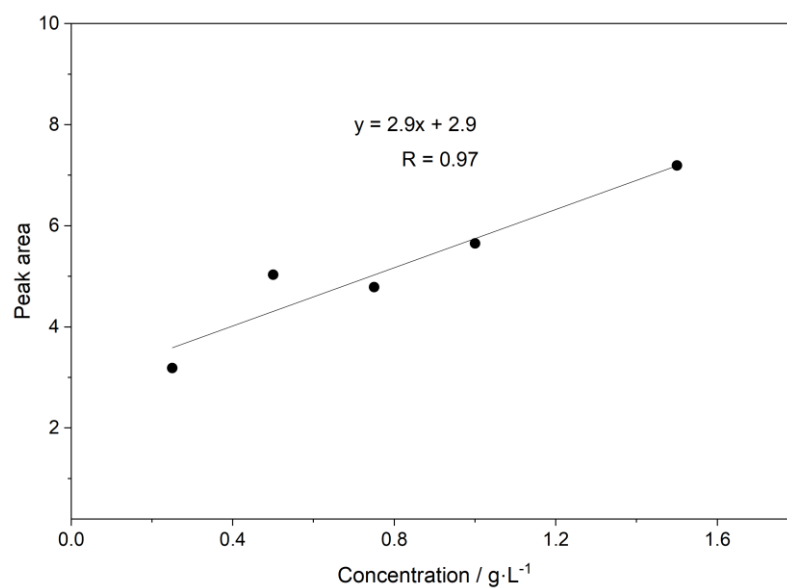
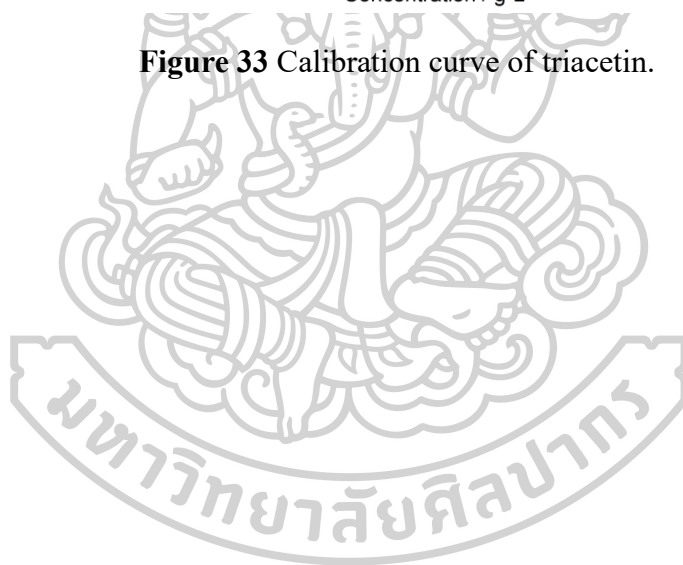


Figure 33 Calibration curve of triacetin.



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