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Heteropoly acid $H_3PW_{12}O_{40}$ as heterogeneous catalyst, and biodiesel production

A graduation research project
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fulfillment of the requirement for the completion of a degree
of Bachelor of science in chemistry.

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Abbreviations

HPAs	Heteropoly acids
CO_2	Carbon dioxide
FAMEs	Fatty acid methyl esters
HPW	Tungsto-phosphoric acid
MTO	Methanol to Olefins

Acknowledgment

First, we thank Allah for the completion of this research, which is a good conclusion to the bachelor's degree. And then to our parents, teachers and university for their efforts and support for us and our future throughout these years, and many thanks to the project supervisor, Dr. Aliyah Alsharif, for her keenness and continuous support for us and for her beautiful giving. Thank you as big as the sky.

Abstract

This project consists of a brief introduction about catalysis field, and presents the physical and chemical properties of tungsto-phosphoric acid HPW, as well as its application on biodiesel production. Also, it describes the proposed mechanism for biodiesel synthesis using HPW catalyst through esterification and transesterification reactions. Literature reviews about biodiesel synthesis by HPW are also provided.

Biodiesel, consisting of long-chain FAMEs (fatty acid methyl esters) is mainly manufactured through esterification or transesterification reactions in the presence of an acid catalyst in homogeneous or heterogeneous conditions. Although there are many studies focused on the use of a homogeneous acid catalyst, equipment corrosion problems and the high energy consumption during separation from the products are considered as major limitations. For all these reasons, heterogeneous acid catalysts are presented as a great alternative given their easy recovery, high reuse potential and low preparation cost which leads to sustainable process.

الخلاصة

هذا المشروع يحتوي على مقدمة موجزة عن مجال الحفز الكيميائي، ويعرض بعض الخصائص الكيميائية والفيزيائية للحفاز الحمضي التنغستوفوسفوريك وكذلك عن كيفية استخدامه في انتاج الديزل الحيوي. كما يعطي توضيح لميكانيكية تفاعل تحضير الديزل الحيوي باستخدام الحفاز الحمضي من خلال تفاعل الاسترة والاسترة التبادلية. اخيراً تم إضافة بعض الدراسات السابقة عن انتاج الديزل الحيوي باستخدام هذا الحفاز.

الديزل الحيوي يحتوي على سلسلة طويلة من الاحماض الدهنية التي يتم تكوينها من خلال تفاعل الاسترة والاسترة التبادلية مع وجود المحفزات الحمضية سواء في الظروف المتجانسة او غير المتجانسة. بالرغم من أن العديد من الدراسات تختص بالمجال الحفزي المتجانس، الا أن مشاكل تآكل المعدات واستهلاك طاقة عاليه خلال عملية فصل الناتج تعتبر من العيوب الهامة. لذلك فان عملية الحفز في الطور غير المتجانس تعتبر طريق بديل ومستدام بدلاً من الحفز المتجانس.

1. Introduction

Catalysts are the backbone of chemical transformations in the industry. Catalytic processes produce around 85-90% of the chemical industry's output [1]. A catalyst provides an alternate, more energetically favorable pathway to the non-catalytic reaction, allowing activities to be carried out at industrially practical pressure and temperature levels [1]. Catalysis is a phenomenon in which the presence of a material alters the rate of a chemical reaction while maintaining its qualitative and quantitative parameters. For a long time, it has been known that the presence of trace amounts of certain substances affects the rate of chemical reactions. Berzelius (1835) coined the term "catalyst" to describe such a chemical and the procedure. A catalyst is a material that, despite its low concentration, alters the rate of a chemical process while remaining chemically unaffected at the end [2]. Catalysts accelerate chemical reactions without changing themselves.

1.1 Importance of Catalysis

A catalyst is an element or a chemical that lowers the activation energy of reactant molecules, allowing a greater number of molecules to collide at a high frequency. As a result of the effective collision, products are formed by overcoming the energy barrier imposed by the activated complex, Figure 1.1. A catalyst speeds up a chemical reaction by forming bonds with the reactant molecules [2]. Generally, catalysts interact with one or more reactants to produce the intermediates that ultimately result in the final reaction product, hence regenerating the catalyst. Catalysts are not consumed during the chemical reaction and hence remain unchanged [2].

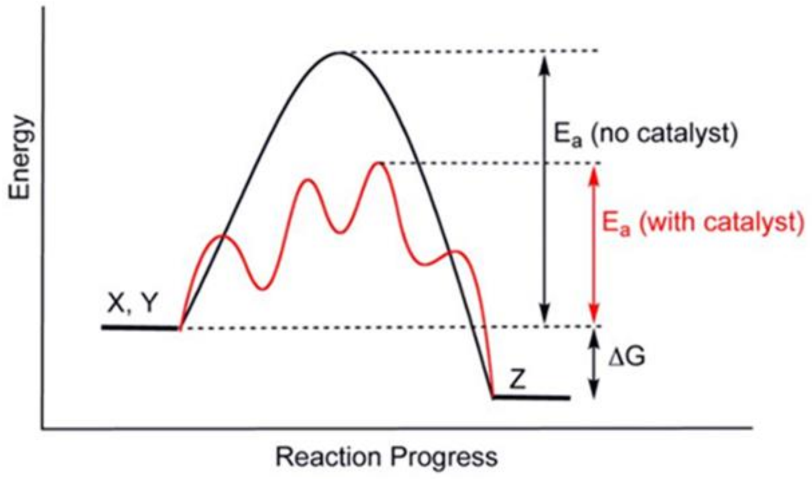


Figure 1.1: Schematic drawing for reaction progress with catalyst and no catalyst [3].

Catalysts have many industrial uses, from the production of food products, biofuels, pharmaceuticals, plastics, and chemicals. Most commercially produced chemicals are made with the help of catalysts. Some notable reactions enhanced by catalysis include production of sulfuric acid used for rust removal as well as a precursor for phosphoric acid, synthesis of ammonia, petroleum refining, and limiting of vehicle emissions. Because of how integral catalysis is to many industrial processes [2]. Catalytic reactions consist of basic phases in which reactant molecules attach to the catalyst, react, and finally detach from the catalyst, liberating it, Figure 1.2.

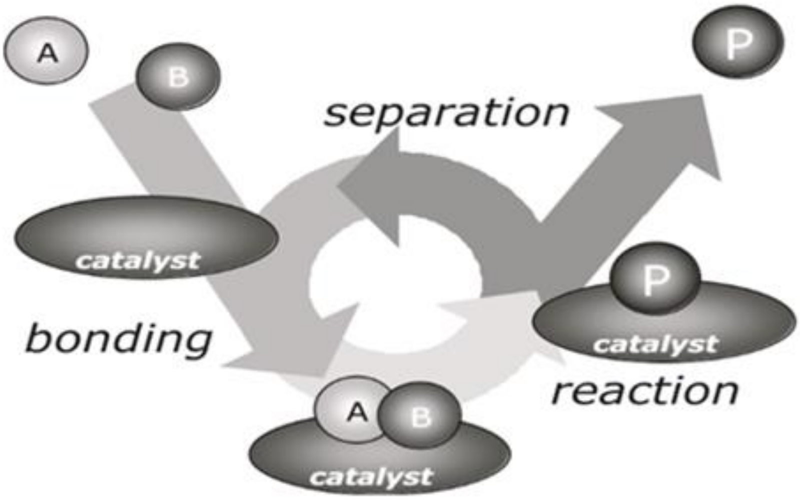


Figure 1.2: Catalytic steps [4].

1.2 Types of catalysis

Important properties of catalytic process have a much lower activation energy than the uncatalyzed reaction, the catalytic reaction proceeds at a much faster rate, creating an alternate reaction route that is clearly more challenging but significantly more energy efficient [4]. Catalysts can be divided into three main types – heterogeneous, homogeneous and biocatalysis. In a heterogeneous reaction, the catalyst is in a different phase from the reactants. In a homogeneous reaction, the catalyst is in the same phase as the reactants. What is a phase? If you look at a mixture and can see a boundary between two of the components, those substances are in different phases. A mixture containing a solid and a liquid consists of two phases. A mixture of various chemicals in a single solution consists of only one phase, because you can't see any boundary between them [5], Figure 1.3. Show more phases, beaker as solid phase and have a gas above the liquid phase, but these phases don't count because aren't a part of the reaction, Figure 1.4.

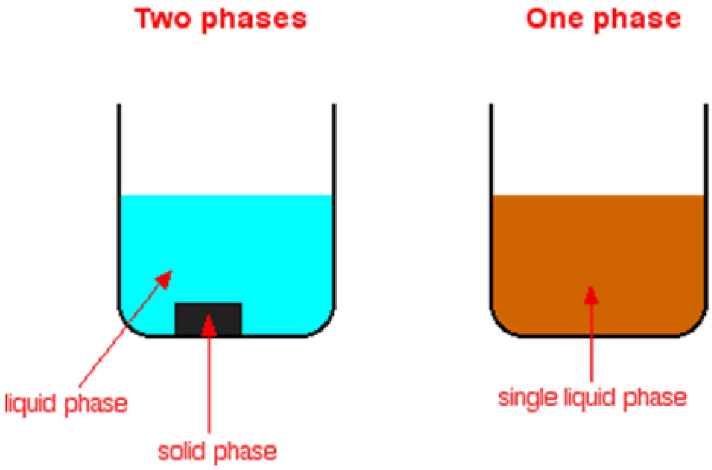


Figure 1.3: Different phases [5].

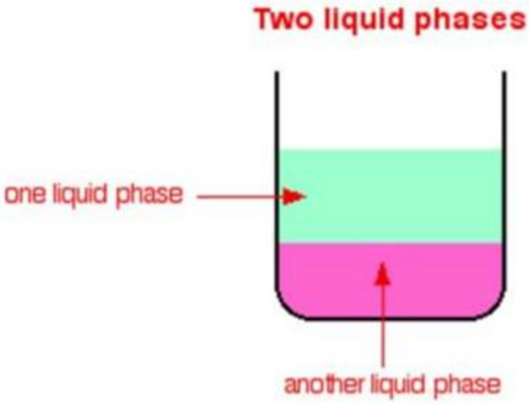


Figure 1.4: Phases of reaction [5].

1.2.1 Heterogeneous Catalysts

Heterogeneous catalysis consists of seven steps as shown in Figure 1.5 [6].

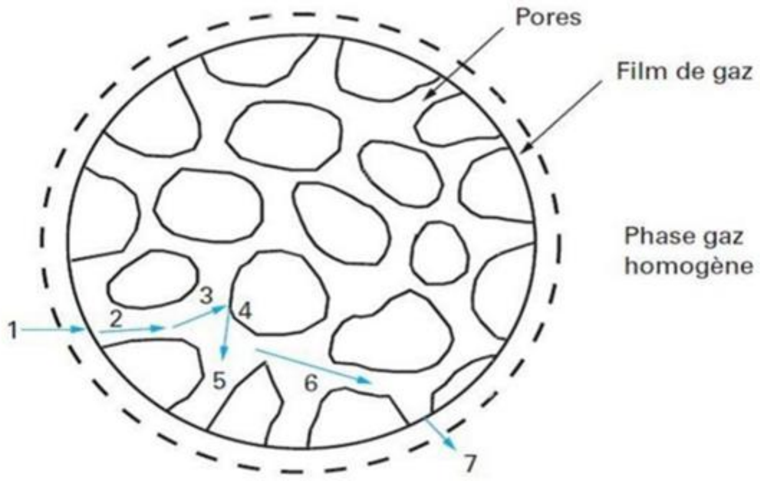


Figure 1.5: The heterogeneous catalytic cycle [6].

1) External transport of substrate molecules by gas phase diffusion to the outer surface of the catalyst (film diffusion).

2) Inward transport of substrate molecules through pores to active sites on the inner surface of the catalyst (pore diffusion).

3) Adsorption of substrate molecules on the surface (chemisorption).

4) Interaction between molecules adsorbed on the surface to form a product (chemical reaction).

5) Product adsorption.

6) Internal transport of product through pores to the outer surface of the catalyst.

7) External transport of product through the boundary layer to the bulk fluid phase [6].

2. Catalysis by $H_3PW_{12}O_{40}$

Catalysis with heteropoly acids (HPAs) and related polyoxometalate systems is a field of growing importance. Several industrial processes based on polyoxometalates catalysis have been developed and commercialized. Due to their unique physicochemical properties, polyoxometalates can be profitably used in homogeneous, biphasic, or heterogeneous systems, providing a broad operational choice. In many cases polyoxometalates provide higher activities and selectivities and allow for cleaner processing compared to conventional catalysts [7]. The majority of catalytic applications use the most stable and easy available Keggin HPAs comprising heteropoly anions of the formula $[X^{n+}M_{12}O_{40}]^{(8-n)-}$, where X is the heteroatom (P^{5+}, Si^{4+}, etc.) and M the addendum atom (Mo^{6+}, W^{6+}, etc.). Show, Figure 2.1 structure of the Keggin heteropoly acid $H_3[PW_{12}O_{40}].6H_2O$. The Keggin structure is composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal-oxygen octahedra MO_6 [8].

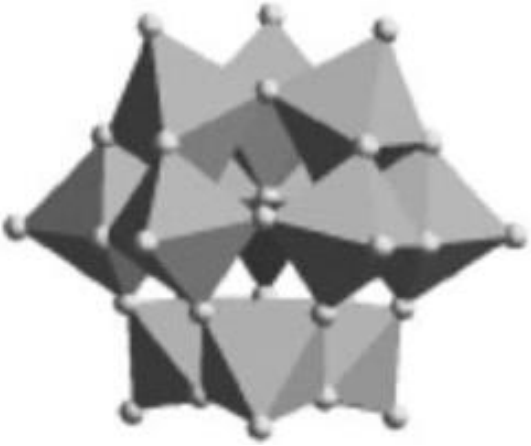


Figure 2.1: The Keggin structure of the $[XM_{12}O_{40}]^{x-8}$ anion [8].

HPAs possess stronger acidity than conventional solid acid catalysts such as acidic oxides and zeolites. The acid strength of Keggin HPAs decreases in the order [9]:

$$H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiMo_{12}O_{40}$$

Usually, tungsten HPAs are the acid catalysts of choice because of their stronger acidity, higher thermal stability and lower oxidation potential compared to molybdenum HPAs [9].

Doubly hydrated protons H^+ $(H_2O)_2$ link four neighbouring anions by forming hydrogen bonds with the terminal W=O oxygens [10], Figure 2.2.

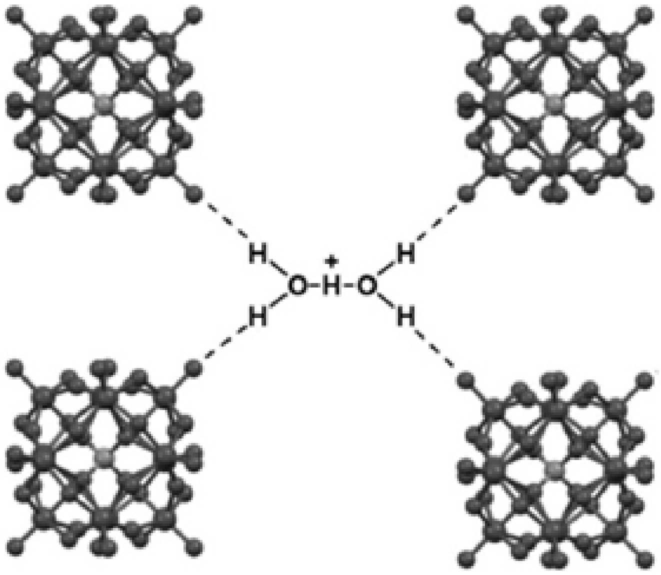


Figure 2.2: Structure of $H_3PW_{12}O_{40}.6H_2O$ [10].

3. Application on heterogeneous catalysis

1) Petroleum Refining [11].

2) Ammonia Synthesis (Haber-Bosch Process) [12].

3) Environmental Pollution Control [13].

4) Hydrogenation Reactions [14].

5) Fischer-Tropsch Synthesis [15].

6) Selective Oxidation Reactions [16].

7) Dehydrogenation of Hydrocarbons [17].

8) Cationic Polymerization and Other Polymerizations [18].

9) Methanol to Olefins (MTO) [19].

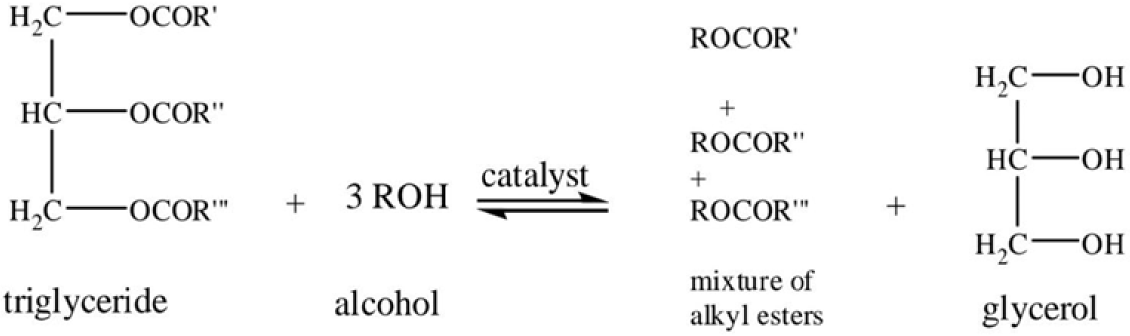
10) Biomass Conversion [20].

3.1 Biodiesel production as an application on heterogeneous catalysis

Biofuel catalysis involves using catalysis to enhance the production of biofuels, which are renewable energy sources derived from organic matter This process improves the efficiency and yield of biofuel production, making it a more viable alternative to fossil fuels. Key types of catalysis in this context include enzymatic, heterogeneous and homogeneous catalysis, each playing a crucial role in converting biomass into renewable energy efficiency [21].

3.1.1 Biodiesel production

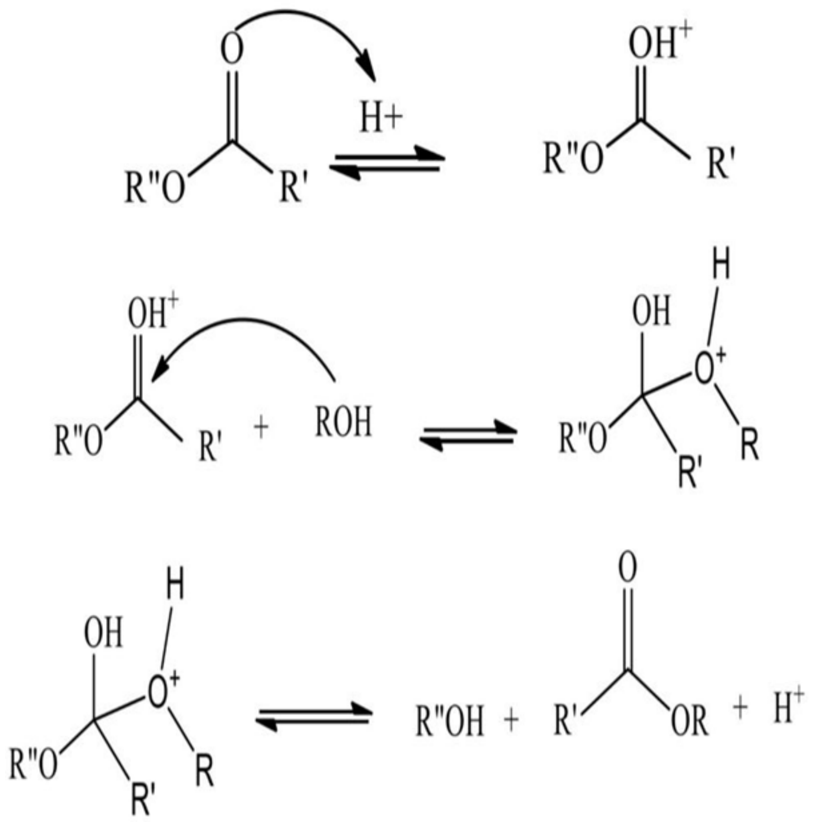
Biodiesel is a renewable fuel comprised of mono alkyl esters of fatty acids. Biodiesel is recognized as a “green fuel” that has several advantages over conventional diesel. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics. Biodiesel is usually produced from vegetable oils and animal fats via their trans- esterification reaction or from free fatty acids via their esterification, Scheme 3.1 [22].



Scheme 3.1: Reaction for oil transesterification [22].

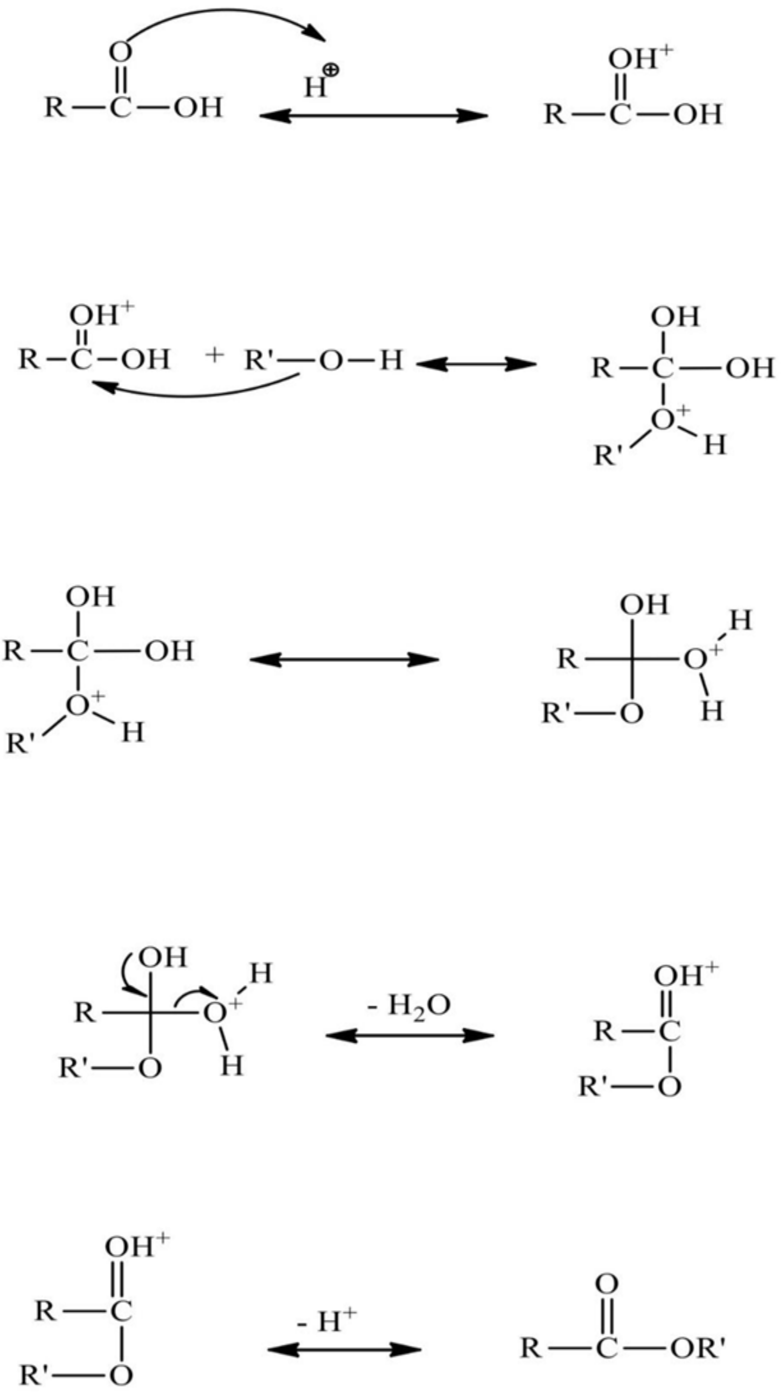
3.2 Reaction Mechanism

Biodiesel production involves chemical reactions occurring under heterogeneous catalytic conditions. Conversion of Triglycerides or free fatty acid oils into biodiesel involves processes that utilize catalysts effectively. These fundamental elements constitute an important stage in the biodiesel production process, requiring a precise understanding of the chemical processes and appropriate operating conditions to ensure product quality and process efficiency. The mechanism of acid catalyzed transesterification involves three steps as shown in Scheme 3.2. The first step is the protonation of the carbonyl group by the acid catalyst. The second step is nucleophilic attack from the alcohol forming a tetrahedral intermediate. In the last step, there is proton migration and breakdown of the intermediate [23].



Scheme 3.2: Mechanism of acid catalyzed transesterification [23].

The mechanism of acid catalyzed esterification is shown in Scheme 3.3. The first step is protonation of the carbonyl group of the acid. The second step is nucleophilic attack by alcohol. The following steps involve proton transfer from one oxygen atom to another one subsequent, elimination of water leads to the protonated ester. Then the catalyst regenerated and soon [24].



Scheme 3.3: Mechanism of acid catalyzed esterification [24].

3.3 Biodiesel goals

Biodiesel is critical to both the environment and the economy. Due to its ability to reduce pollutants and greenhouse gas emissions, producing a heterogeneous biofuel catalyst is considered an optimal choice, as it is an environmentally friendly and renewable resource. It is highly suitable for diesel fuel because of its exceptional qualities and advantages. Biodiesel delivers 4.5 times more energy than fossil fuels and has a chemical composition and content similar to conventional diesel. It reduces cancer-causing chemical emissions by approximately 85%, making it less harmful than traditional diesel fuel [25]. Additionally, it is free of sulfur, hydrocarbons, and polycyclic aromatic hydrocarbons, and it is biodegradable [25].

3.4 Advantages of biodiesel

1) No vehicle modification or any fueling equipment needed.

2) power, performance and economy: proven power generation, performance and cost efficiency made biodiesel a useful fuel.

3) Effect on environment: biodiesel is health by lowering the emissions of CO_2 which reduces the effect of global warming.

4) Biodiesel is safer to handle because it is less toxic and easy to store than petroleum.

5) Biodiesel helps communities by keeping energy dollars at home [26].

4. Previous studies about biodiesel production

Heteropoly acids are widely used for acid catalyzed reactions for biodiesel production. Heterogeneous solid acid catalysts, promote transesterification and esterification reaction from low-quality, unrefined feedstock without any side reactions. It was reported that HPAs exhibited high activity for biodiesel production in homogeneous or heterogeneous system supported on SiO_2, Ta_2O_5, ZrO_2, or other supports [27].

Sudhakar and Pandurangan [28], reported that for producing biodiesel via transesterification of neem oil with methanol using a various weight percentage of $H_3PW_{12}O_{40}$ (10, 20, 30%) was impregnated on KIT-6 and it was characterized by different physicochemical techniques. Moreover, its catalytic activity was examined by liquid-phase transesterification of neem oil under different experimental conditions. Among the different wt% catalyst, 20% catalyst showed highest neem oil conversion and selectivity at an optimized reaction temperature of 60 °C. Further, the spent catalyst was recovered and recycled three times, and it showed activity losses of less than 4%.

Patino et al. [29], studied the catalytic performance of Phosphotungstic acid (HPW) and silicotungstic acid (HSiW) as homogeneous and as heterogeneous catalysts after supported on graphite –HSAG500-, montmorillonite –MMT- and alumina –Al_2O_3. Both catalysts exhibited similar performance in homogeneous phase, with slightly higher biodiesel yield for HPW. When the different supports were tested with HPW, the maximum yield obtained follow the trend: MMT > HSAG500 > Al_2O_3, but a greater leaching of the heteropoly acid (HPA) was observed with MMT.

Kurhade and Dalai [30], reported that MAS-9 aluminosilicate (HPW-MAS-9 composite with 25 wt% HPW loading) had shown a promising catalytic activity for methyl ester synthesis from unrefined green seed canola oil. Also, the composite catalysts can be used multiple times without any leaching of the HPW or loss of reactivity, thus, making them potentially efficient heterogeneous catalysts. Also, they investigated the kinetics and gain insights into mechanistic details of the transesterification reaction using this HPW-MAS-9 composite catalyst.

Fioravante et al. [31], used cesium-modified phosphotungstic acid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) as a heterogeneous catalyst for transesterification of canola oil with methanol. The canola oil conversion reached 55% at room temperature after 24 h. The reusability tests showed that the conversion of canola oil to biodiesel was maintained.

5. Conclusion

The use of HPA heterogeneous catalysts for biodiesel production reactions is promising as far as the catalysts are easily separated from the reaction media and prove to be reusable. Therefore, the production of biodiesel via transesterification providing environmentally friendly option for hazardous synthetic pathways**.**

Low surface area of HPW limits their application in biodiesel production. However, HPW supported on solid carriers provided good results based on biodiesel yield, by improving their catalytic activity by increasing the available active sites on surface area.

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