

Review

Not peer-reviewed version

Lewis Acid-Base Site Assisted In-Situ Transesterification Catalysis to Produce Biodiesel

Zhuangzhuang Zhang , [Pan Meng](#) , Hangyu Luo , Zhengfei Pei , [Xiaofang Liu](#) *

Posted Date: 4 September 2024

doi: 10.20944/preprints202409.0225.v1

Keywords: Biodiesel; microalgae; transesterification; catalyst; Lewis acid-base catalyst



Preprints.org is a free multidiscipline platform providing preprint service that is dedicated to making early versions of research outputs permanently available and citable. Preprints posted at Preprints.org appear in Web of Science, Crossref, Google Scholar, Scilit, Europe PMC.

Copyright: This is an open access article distributed under the Creative Commons Attribution License which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Disclaimer/Publisher's Note: The statements, opinions, and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions, or products referred to in the content.

Review

Lewis Acid-Base Site Assisted In-Situ Transesterification Catalysis to Produce Biodiesel

Zhuangzhuang Zhang, Pan Meng, Hangyu Luo, Zhengfei Pei and Xiaofang Liu *

Key Laboratory of Surveillance and Management of Invasive Alien Species in Guizhou Education Department, College of Biology and Environmental Engineering, Guiyang University, Guiyang 550005, China.

* Correspondence: liuxfzap@163.com(X.L.); Tel.: +86 13984348707(X.L.).

Abstract: Biodiesel, a potent replacement for petroleum diesel, is derived from fatty acids in biomass through transesterification, which is renewable, non-toxic, and biodegradable and is a powerful replacement for petroleum diesel. Lewis acid has been proven effective for esterification and transesterification. The Lewis base enhances the electrophilic and nucleophilic properties of the molecules that bind to it, leading to the remarkable versatility in the Lewis base catalytic reaction. Many studies have shown that Lewis acid/base catalyzed in-situ transesterification is a fast and environmentally friendly method for producing biodiesel. The utilization of Lewis acid-base sites to catalyze transesterification has been shown to enhance their efficiency and utilization of acid-base active sites. This review explores biodiesel production by different catalysts using Lewis acid-base sites, the conditions for catalytic transesterification, the effects of different reaction parameters on biodiesel production, and biodiesel production process.



Keywords: Biodiesel; microalgae; transesterification; catalyst; Lewis acid-base catalyst

1. Introduction

Biodiesel, a sustainable energy source, has always been regarded as a potential substitute for oil. Transesterification is the primary method for producing biodiesel from natural biomass fats. Biodiesel production typically consists of two parts: lipid extraction and transesterification; transesterification usually involves a chemical reaction between lipids and methanol or ethanol [1]. However, there are more efficient ways to produce biodiesel than this method as additional steps are required. The in situ transesterification method has two steps of lipid extraction and transesterification simultaneously. In situ transesterification method, which has two steps of lipid extraction and transesterification at the same time [2]. In producing lipids from plants, wastes, and other biomass, selecting dried biomass is beneficial for pretreatment [3,4] and breaking down biomass into small molecules as much as possible. For example, lipids in microalgae are concentrated

in the cell [5]. The cell wall needs to be broken to release lipids. Pretreatment brings higher energy consumption, such as heating and mechanical shredding, which hinders the economic development of biodiesel. In situ transesterification can directly use wet biomass, such as microalgae salvaged from water, to produce biodiesel through a one-pot process, significantly improving production efficiency and reducing the energy consumption of drying microalgae [6]. In -situ transesterification involves strong acids, such as sulfuric acid and nitric acid. It is not only accessible for the production equipment, but the excess acid in the oil also must be removed to make the resulting biodiesel up to the standard [7]. Lewis acid has higher reaction activity than traditional strong acids and can be transesterified under mild conditions [8].

Alkaline catalysts are also essential catalysts for transesterification, as they are easily obtained and inexpensive [9]. Alkaline hydroxides and methanol used in commercial biodiesel plants are efficient and short in time but require the saponification of catalysts and lipids and require more water in the washing process. Homogeneous catalysts, such as alkaline hydroxide and alkaline methanol (NaOCH_3 and KOCH_3), can cause soap formation. Homogeneous alkali catalysts have many disadvantages, such as difficult separation from products, poor recycling ability, and will produce much polluted water, which increases production costs [10]. The study of heterogeneous alkaline catalysts reduces the shortage of catalysts [11]. It is said that the alkaline catalyst has vigorous catalytic activity because it has Lewis basic sites [12], and the surface positions of anionic oxides and hydroxides can serve as Lewis bases. Their strength will depend on the properties of cations and their local environment. The Lewis basic sites of many different catalysts can catalyze transesterification [13–15]. Lewis acid-base sites are widely used in heterogeneous catalysts [16], while double active sites with Lewis acid-base sites are also used to enhance the conversion of compounds [17]. This review summarizes the current advanced Lewis acid/base and double active site catalysts and how they are used in in-situ transesterification to produce biodiesel. Finally, we address the current limitations and challenges of these catalysts and outline effective and practical optimization conditions to enhance catalytic effectiveness.

2. Transesterification of Biodiesel

2.1. Fatty Acid Composition and Properties of Biodiesel

Biodiesel is a mixture of monoalkyl esters obtained through the reaction of lipids (triglycerides) with short-chain alcohols in the presence of catalysts [1,18]. Triglycerides are one of the main components of biomass oil. However, there are other lipids related to fatty acid ester bonds in its composition, such as phospholipids, glycolipids, and sphingolipids, all of which are saponified lipids. In the presence of excess methanol or ethanol, triates produce fatty acid methyl esters (FAME) through transesterification reactions that can be catalyzed by acids or bases. In addition, there are a lot of free fatty acids (FFAs) in natural biomass oil [19]. Under ideal conditions, FAME content in biodiesel is 100%, but there are impurities in biodiesel caused by low conversion rate and difficult separation [20], such as glycerol, monoglyceride, and diglyceride. Both fresh wet biomass and recycled biological waste contain a significant amount of FFAs, and FFAs can also hinder the transesterification reaction [21]. Usually, homogeneous or heterogeneous catalysts are used for esterification to reduce FFAs content to less than 2% before transesterification [22]. The traditional catalyst for the esterification of FFAs to FAME has a high reaction temperature and wastes much energy [23,24]. Currently, some new catalysts are changing this situation [25].

2.2. Research Status of Acid-Base Catalyzed Transesterification

Transesterification is a reversible reaction in which alkyl groups of triglycerides are exchanged with alcohol, also known as alcoholysis. Transesterification is a reversible reaction that involves exchanging alkyl groups of triglycerides with alcohols, also known as alcoholysis [26]. For instance, in Figure 1, The oil (triglycerides) reacts with methanol to form ditriglycerides and methyl esters, and the reaction continues to form monotriglycerides and methyl esters. Monoglycerides react with methanol to form glycerol and methyl ester.

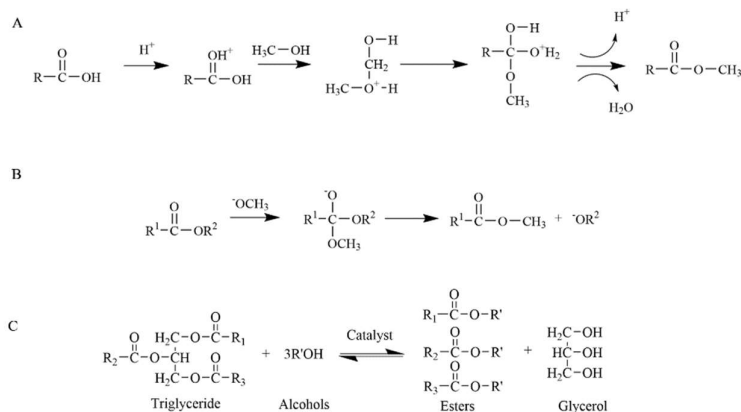


Figure 1. (a) Acid catalyzed esterification reaction, (b) alkali-catalyzed esterification reactions, (c) transesterification of triglycerides.

Under ideal conditions, 1mol triglyceride reacts with 3 mol alcohol to form 3mol FAME and 1mol glycerol. However, in the case of improper control of the conditions, there will be a side reaction to the transesterification reaction, resulting in the oil being saponified with alkali. Acid catalysts, in the presence of acidic catalysts, esterify FFAs with methanol to form methyl esters, acidic catalysts are suitable for catalyzing raw materials with high-acid raw materials[27]. The most classical homogeneous acid catalysts include sulfuric acid, phosphoric acid, and para-toluenesulfonic acid. The reaction vessel was filled with 1:10 volume of methanol and then chloroform, hexane, or petroleum ether were added to the container for the extraction of FAME after transesterification. The reaction mixture was heated above 90 °C for 0.5-3 h, and then the extraction layer containing FAME was centrifuged to obtain biodiesel [28].

When an alkali catalyst is used, FFA neutralization with triglycerides occurs in the presence of water. Alkali catalysts and alcohol produce alkali alkoxide and water, which is beneficial for hydrolysis and saponification. Some studies [29] suggest that the level of moisture in bio-oil also affects the choice of catalysts. If there is more water, it is suitable for acid-catalyzed transesterification. If the moisture is low (less than 3.0%), alkali-catalyzed transesterification is recommended. Alkali catalysis consists of three consecutive reversible reactions. In the reaction sequence, a triglyceride molecule is converted to diglyceride, monoglyceride, and finally glycerol [18]. In the industry, basic catalysts are more commonly used than acid catalysts due to their higher activity and lower process temperature than acid-catalyzed transesterification [30]. To use homogeneous alkali catalysts, the pH value needs to be neutralized to extract crude biodiesel more efficiently. The pH value of the mixture and the methanol content determine the extraction efficiency [31]. The extraction methods for crude biodiesel after transesterification include wet cleaning, dry cleaning, and membrane extraction [32]. Heterogeneous solid base catalysts can easily be separated from the reaction mixture without the need for water[31]. They are easy to regenerate and less corrosive, resulting in safer and cheaper, so currently, heterogeneous basic catalysts, including solid bases, are widely used [33,34], metal supported solid bases [35], metal oxide supported solid bases [36], basic catalysts based on metal organic frameworks (MOF) [37], and more.

3. Lewis Acidic Catalyst

Lewis acid are substances that lack electron pairs in the valence orbitals and therefore can accept electrons. Due to the presence of electron-deficient metal centers, they activate electron-rich substrates [38]. The higher acidity of the Lewis acid catalyst is conducive to improving the conversion rate of transesterification. In the acid transesterification reaction catalyzed by Lewis acid, the oxygen connection of the acid site with the carbonyl group of triglyceride / FFAs increases the electrophilicity of adjacent carbon atoms, making them more vulnerable to nucleophilic attack [39]. It goes through four steps: (1) forming carbonyl carbon cationic electrophilic reagents by Lewis acid; (2) nucleophilic

attack of alcohols on carbon cations and the formation of tetrahedral intermediates; (3) proton transfer and breakdown of intermediates; and (4) formation of FAMES and the regeneration of catalysts. The formation of strong electrophilic reagent between Lewis acid and triglyceride is the key factor.

3.1. Research Status of Lewis Acidic Catalyst

AlCl_3 and ZnCl_2 can be directly mixed with biomass-oil and react, so they can be used as homogeneous Lewis acid catalysts [40]. These catalysts are inexpensive and easy to prepare. However, the reaction rate of these catalysts is very slow. Abraham Casas et al. carried out transesterification of sunflower oil with a ZnCl_2 catalyst/oil ratio is 0.15 mol/mol at 150 °C for one hour, and the methyl ester content was only 76.7% by weight. In addition to the ester exchange reaction, an esterification reaction was also carried out at the same time. After 1 hour of reaction at 150 °C, the FFAs in the reactant decreased by 60%. It has been proven that the Lewis acid catalyst has two catalytic abilities of esterification and transesterification, and biomass raw materials containing more fatty acids such as waste vegetable oil can be used. One way to improve the transesterification efficiency of AlCl_3 and ZnCl_2 is to use cosolvent. Nestor et al.[41] use Tetrahydrofuran(THF) as a cosolvent. The addition of THF reduces the mass transfer problems commonly encountered in heterogeneous systems. In the same phase of AlCl_3 and triglyceride, the activation of carbonyl carbon is more favorable, resulting in higher conversion. Guan et al. [40] used CO_2 as cosolvent, AlCl_3 was dissolved in ethanol and 5 MPa CO_2 co-solvent, and the conversion reached more than 90% within 1 hour at 180 °C. It has been found that AlCl_3 can also be used as a flocculant to collect microalgae and other biomass from natural water bodies or sewers, which will combine upstream and downstream operations.

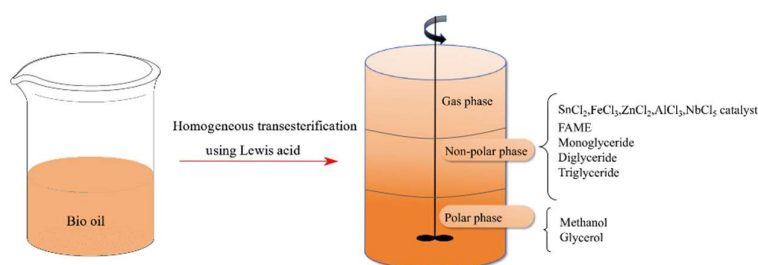


Figure 2. In situ transesterification and recovery of Lewis acid catalyst.

Divalent cations are catalysts for transesterification and esterification. Some reports use divalent metal acetate as a transesterification catalyst and metal carboxylates such as acetate and stearate as catalysts [42–44]. Some carboxylic acids, such as zinc laurate, zinc palmitate, zinc stearate, etc., are soluble in the reaction medium at 100 °C and rapidly recrystallize at room temperature, reducing the mass transfer resistance during the reaction process and separating them from the reaction medium. The ease of recovery from reactant media makes it a unique advantage.

3.2. Heterogeneous Lewis Acidic Catalysis

Lewis acid has the advantage of reducing equipment corrosion, particularly heterogeneous catalysts, solid Lewis acid, and immobilized catalysts, which not only ensure the catalyst's recycling in the reaction but also help maintain its long-term activity of the catalyst[38,45]. Common solid Lewis acid catalysts such as metal oxides, molecular sieves, ion exchange resins, etc. Vinicius et al. [46] effects of several metal oxide catalysts on esterification yield under different reaction conditions was studied. Metal oxides, especially alumina and tin oxide, have great potential for producing biodiesel with conversion rates of 80-90%.

Sulfated metal oxide is an effective acid heterogeneous catalyst. Rodrigo Zunta Raia et al.[47] prepared biodiesel from jatropha curcas oil through simultaneous esterification and transesterification with sulphated zirconia. The sample with the highest acidity had the highest catalytic activity, resulting in an ester yield of 59.4%. Du et al.[48] is doped with tin oxide through hydrothermal synthesis of sulfated silica. SiO_2 can be highly dispersed in sulfated tin oxides, which contributes to the formation of strong acidic sites in sulfated tin oxides. The catalytic experiments show that tin oxide doped with sulfated silica has higher activity than traditional tin sulfate in the transesterification of triglyceride with methanol. However, the issues of poor stability and low catalytic efficiency of sulfur metal oxides have not been fully resolved. Zn / Sn catalysts supported by modified metal oxides with catalytic activity have potential prospects. Li et al. [49] studied the interaction between Zn and ZrO on a zirconia-supported zinc catalyst. The introduction of Zn species can significantly improve the acidity of the catalyst. Compared to the catalytic activity of different Zn supported ZrO_2 , it was found that 7% Zn / ZrO_2 catalyst had the best catalytic activity for biodiesel and had good selectivity. The Lewis acid catalyst is immobilized to form a heterogeneous catalyst, effectively eliminating or significantly reducing the use of harmful substances and their production in the chemical reaction process [50]. Polyoxometalates (POMs) are anionic clusters composed of various metal oxides, which have significant functions in the catalytic field. By introducing Lewis acid sites on the backbone of POMs, these compounds can play a catalytic role in esterification reactions. To improve catalytic efficiency, POMs are often dispersed on various solid supports, including silica, zirconia, carbon materials, titania, alumina, and porous silica. This dispersion method can effectively expand the surface area of POMs, thereby increasing the number of catalytically active sites thereby improving catalytic performance [51]. Mirit et al. [45] successfully immobilized Lewis acids into a sol-gel matrix and immobilized Lewis acids (BF_3 and AlCl_3) in a silica matrix as catalysts, allowing their reuse and reuse in continuous biodiesel production. M.A.A. Aziz et al. [52] prepared WO_3 supported on silica mesoporous-macroparticles catalyst and studied the effect of WO_3 loading on FAME catalytic activity. Under optimal reaction conditions determined by the response surface methodology (RSM), the biodiesel conversion rate was 96%. The catalyst exhibits excellent catalytic performance is attributed to the high Lewis acid site content and pores within and between the catalyst particles. This structure provides efficient transport for reactants and products and significantly improves the efficiency of the entire catalytic reaction. Carbon nanotubes (CNTs) with their high thermal conductivity, accessibility to the active phase, have good chemical stability, and have a high specific surface area in corrosive media hold great promise as catalyst carrier. The wall defect structure of multi-walled carbon nanotubes (MWCNT) contributes to forming more Lewis acid active sites [53–55]. The preparation of sodium oxide impregnated on CNTs by Mohd et al.[56] and as a heterogeneous catalyst for transesterification of waste edible oil, with the positive metal ion Na (cation) having Lewis acidity, enhances the electronegativity of oxygen O^{2-} (anion) adjacent oxides, improving the alkaline strength of the catalyst. Shu et al. [55] prepared the solid Lewis acid catalyst, $\text{Al}^{3+}\text{-SO}_4^{2-}$ / MWCNTs. The acid sites are primarily made up of Lewis acids. During the reaction process, the catalytic temperature is reduced, and the quality of the catalyst and reactants is relatively low. The conversion rate of FAME can reach 95%. Metal organic frameworks (MOFs) are a particular type of coordination polymers composed of metal ions and organic ligands [37]. MOFs have large porosity, uniform pore size, controllable functional groups, and structural durability, making them an ideal choice for synthetic transesterification/esterification catalysts. Hasan et al. [57] used sulfonic acid functional ligands to hydrothermally synthesize highly porous and acidic MOFs, namely MIL-101 (Cr)- SO_3H . Under microwave irradiation, it only took 20 min for MIL-101 (Cr)- SO_3H

to achieve a 93% yield of methyl oleate. The catalyst can also be used under heating, but it takes 10 h to achieve the same yield. After thermal filtration, the catalyst's yield slightly decreases before the third operation, demonstrating its reusability.

3.3. Lewis Acidic Ionic Liquids and Deep Eutectic Solvents

As a developing material, ionic liquids (ILs) have garnered attention due to their unique characteristics. Their thermal stability and recyclability are their main highlights. Introducing adjustable Lewis acid/Brønsted acid sites to ionic liquids enhances the catalytic activity and selectivity of ILs [58]. ILs play an essential role as catalysts in converting biomass oil to biodiesel, especially when they are designed to contain Lewis and Brønsted acid sites. The advantages of this method including ease of operation, low corrosiveness, recyclability, high yield, low cost, no saponification process, and reduced waste generation[59], offer a promising outlook for the future of renewable energy.

Panchal et al. [60] synthesized ILs, 3-(N, N-dimethyldodecyl ammonium) propane sulfonic acid p-toluene sulfonate ([DDPA] [Tos]) for the transesterification of soybean oil into biodiesel. Under optimal conditions, the yield of biodiesel reaches 75%. The new ILs can be reused at least 6 times, and the conversion rate will not be significantly reduced. After 6 runs, the catalyst's recovery rate reaches 68%, showing stable reusability. Han et al. [61] synthesized Brønsted-Lewis acidic ILs composed of [SO₃H-pmim] Cl and Sn (II), which was used in the catalytic transesterification of soybean oil with methanol to prepare biodiesel. The coexistence of Brønsted acid and Lewis acid also ensures the enhancement of catalytic activity. The presence of Sn²⁺ in the catalyst system plays a crucial role, as it tends to combine with the carbonyl oxygen of unsaturated fatty acids (showing strong electronegativity) to form intermediate complexes. This process promotes the effective interaction between the carbonyl carbon and methanol oxygen atoms, thereby enhancing the catalytic activity. At the same time, the existence of Brønsted acid proton (H⁺) may couple with carbonyl oxygen, resulting in the decrease of negative charge, which is beneficial to the release of Sn²⁺ and the formation of biodiesel. Xie et al. [62] modified Polyoxometallate (POM) hydrochloric acid with a Keggin structure using UiO-66-2COOH, a MOF material and then coordinated the modified POM anion with ILs cations with functional groups. Finally, the sulfonated acidic ILs were integrated into the prepared POM/UiO-66-2COOH composite structure. The prepared AILs/POM/UiO-66-2COOH solid catalyst has a high surface area and acidity. When the ratio of methanol to oil is 35:1, and the amount of catalyst is 10 wt%, for 6 h, the reaction temperature is 110 °C, and oil conversion is 95.8%. The intense interaction between -SO₃H and POM can effectively prevent the loss of active components from the MOF carrier, ensuring the stability of the active components of the solid acid catalyst. This stability provides a sense of reassurance and confidence in the reliability of the catalyst. In addition, composite catalysts containing HPW and sulfonic acid groups showed better recycling performance. Hence, the strong interaction between HPW and -SO₃H groups not only increases the acidity of the catalyst but also prevents the loss of active substances from the MOF carrier.

Deep eutectic solvents (DES), a type of ILs, are a promising green solvent with unique properties. Their low cost, simplicity of preparation process, non-toxicity, and biodegradability make them a superior alternative to ILs [63]. DES have the potential to compensate for the lack of traditional liquid acid and solid superacid. They can be prepared by mildly mixing of hydrogen-bonded acceptor (HBA) and hydrogen-bonded donor (HBD), creating a wide range of hydrogen-bonded connections are constructed. Typically, DESs are composed of two or more components with a melting point lower than any single component [64]. The strong hydrogen bond acceptability and high acid strength of these chlorides leads to the formation of an extensive hydrogen bond network formed in DES. This network efficiently contacts biomass and promotes the deconstruction of biomass structure through intensely competitive hydrogen bond interaction[65,66].

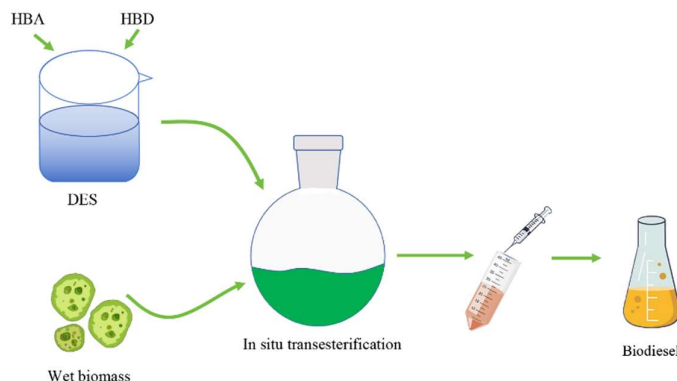


Figure 3. Biodiesel was obtained by DES in situ transesterification.

Liu et al. [67] prepared DES with ChCl and *p*-toluenesulfonic acid as HBA and HBD. DES, composed of choline chloride and *p*-toluenesulfonic acid, not only has catalytic activity similar to that of the original *p*-toluene sulfonic acid but also has good solvent performance. In particular, the *p*-toluenesulfonate DES group can be easily separated from the reaction system. Under the conditions of mixing *p*-toluenesulfonic acid and ChCl in a molar ratio of 1:3, using a certain amount of DES as a catalyst, the molar ratio of methanol to lipids is 8:1, the reaction temperature is set to 110 °C, and the reaction lasts for 2 hours, the conversion rate of the transesterification reaction can reach 98.66%. Ngatcha et al. [68] prepared ChCl-ZnCl₂ DES and ChCl-SnCl₂ DES. The study on the geometric structure of DES is a result of collaborative research. It reveals that the bond length of Sn-Cl is higher, and the charges of Zn and Sn atoms are 0.567 ~ 0.668 and 0.878 ~ 0.883e, respectively. Despite being the metal center farthest from the choline part, it exhibits the most vigorous acidity, making ChCl-SnCl₂ DES more acidic. Alam et al. [69] proposed a hypoeutectic solvent using Lewis acid (ChCl-CrCl₃·6H₂O). The FAME content of the biomass treated by Brønsted acid DES and the catalyst at 120 °C 5 % methanol solution, and 5 mL solvent volume reached 39.86 mg/g.

4. Lewis Basic Catalyst

Homogeneous base catalysts have been widely used in the esterification process of biodiesel. However, there are some limitations in their practical use, such as difficulty in separating the catalyst from the product after the reaction, formation of corrosive wastewater, and saponification problems that quickly occur during the reaction process, limiting their more comprehensive application. Using the Lewis basic site, the catalyst loaded with Lewis basic site has the function of transesterification catalysis, which has more advantages than a homogeneous strong base catalyst in recycling and reducing waste pollution [34,70]. The Lewis alkaline site is fixed by new materials such as MOFs to form a solid alkaline catalyst, which can enhance the catalytic effect of the Lewis alkaline site, improve the catalyst's stability, and increase the number of reuses of the catalyst [71–75]. Using homogeneous basic catalysts requires secondary processing and purification steps to isolate the catalyst from the reaction product. Conversely, heterogeneous catalysts are easily removed from the reaction mixture, making the purification step easier.

4.1. Research Status of Lewis Basic Catalysis

The influence of the Lewis basic site on the transesterification catalytic activity of the material is complex, mainly due to the location of the basic site and the crystal structure of the catalyst [76]. The CO₂ chemisorption spectra of the catalysts were analyzed by CO₂-temperature programmed desorption (CO₂-TPD) to distinguish the contribution of alkaline sites with different strength characteristics [77]. The basic sites of catalysts come from different sources. We have identified several main types of basic sites, including solid alkaline metal catalysts, alkaline earth metal oxide, siloxyl anion, Al₂O₃, SiO₂, and hydrotalcite doped with alkali metals, alkali metal nano-material.

4.2. A Solid Alkali Metal Catalyst

Cui et al. [78] using $\text{KF}/\gamma\text{-Al}_2\text{O}_3$ catalyst prepared by KF and Spherical $\gamma\text{-Al}_2\text{O}_3$ calcined in air at 600 °C the molar ratio of methanol to oil was 12:1, the amount of catalyst was 4%, and the temperature was 65 °C The biodiesel with the best performance was obtained. Giovanni et al. [79] studied the transesterification of triglycerides catalyzed by NaAlO_2 (SA) to produce biodiesel. There are weak and strong basic sites on the catalyst's surface. Compared to other alkali metal catalysts, the performance of SA is significantly better, although the difference in the number of bases is not significant, it is generally believed that the higher the basicity, the higher the yield of biodiesel, indicating that SA has a more robust alkaline site. Singh et al. [80] phosphotungstic acid (TPA) on graphene oxide (GO) using the impregnation process, and a series of potassium-supported TPA/GO ($\text{K}/\text{TPA}/\text{GO}$) catalysts were prepared through a wet impregnation process. K impregnation increases the number of active sites (alkalinity), thereby increasing activity. Metal ions (TPA) on the surface of mixed metal oxides may lead to weak acid sites. K and TPA are applied to GO to create basic and acidic sites, respectively. In the high FFAs transesterification procedure, the two steps of esterification and transesterification occur simultaneously on the catalyst surface. These findings have the potential to revolutionize the field of biodiesel production.

4.3. Alkaline Earth Metal Oxide Catalyst

Solid bases contain a variety of catalysts, such as alkaline earth metal oxides. CaO , MgO , SrO , and BaO are all catalysts with significant catalytic effects. Alkaline earth metal oxides are common solid alkaline catalysts that are easy to prepare due to their availability, non-toxicity, reusability, low cost, and high concentration of surface alkaline sites that provide activity [81]. Cabrera et al. [82] incorporated Ce into the ZnAl hydrotalcite structure and modified its basicity, using it as a catalyst for soybean oil transesterification. MgAl-Ce (X) hydrotalcite is activated at high temperatures to produce intermediate and strong alkaline sites, which can be transesterified at 67 °C The yield of FAME is 90%. Wang et al. [83] have synthesized an innovative, walnut-shaped composite catalyst derived from industrial by-products, incorporating calcium oxide and cancrinite. This novel catalyst, with its unique shape and composition, has the potential to significantly improve the efficiency of the transesterification process. Analysis via CO_2 temperature-programmed desorption ($\text{CO}_2\text{-TPD}$) techniques revealed that CO_2 release is attributed to various basic sites with differing strengths: weak, moderate, and strong. These sites are associated with hydroxyl groups ($-\text{OH}$), the O^{2-} anion within the $\text{Ca}^{2+}\text{-O}^{2-}$ linkage, and the less coordinated O^{2-} anion. The temperature at which pyrolysis occurs is a pivotal factor that affects the configuration of calcium within the catalyst, ultimately affecting its alkalinity and the strength of its basic properties. The catalyst's elevated basic potency and intensity confer superior catalytic efficacy in the transesterification process involving methanol. Under optimal conditions, a temperature of 70 degrees Celsius, a duration of 3 hours, a catalyst concentration of 6.0 weight percent, and a methanol-to-oil molar ratio of 10:1, FAME can yield 95%.

Singh et al. [84] synthesized barium zirconate through a coprecipitation method for transesterification. Despite its low specific surface area, barium zirconate has high activity under suitable reaction conditions. The total alkalinity of barium zirconate is 1.21 mmol/g. The Lewis base on mixed metal oxides is the main reason for the alkaline strength of the catalyst. Under optimized transesterification conditions, the FAME conversion was $98.79 \pm 0.5\%$. What's particularly promising is that the barium zirconate catalyst was recovered and recycled 9 times without any significant activity loss.

Alongside the prepared catalysts, those derived from natural rocks are potential alkaline earth metal-based catalysts for transesterification. Wang et al. [85] selected åkermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) from silicate ores for biodiesel transesterification. The $\text{CO}_2\text{-TPD}$ data indicate that the åkermanite basic site's concentration reaches 0.8822 mmol per gram. When the catalyst's mass percentage is set at 20%, with a methanol-to-oil molar ratio of 10:1, and the reaction proceeds at a temperature of 190 degrees Celsius over 6 hours, the FAME conversion rate impressively reaches 99%. Even after 16 consecutive catalytic cycles, the conversion rate remains robust at 85%, demonstrating the catalyst's remarkable durability and stability.

SiO₂ with alkaline sites have been proven to be an attractive catalyst for transesterification. By hybridizing the structure and morphology of SiO₂, materials with different phases, tissue levels, and morphologies are controlled to achieve the transesterification of alcohols [86]. The catalytic activity of silica is due to the siloxyl groups ($\equiv\text{SiO}-$) formed in its structure, which promote the deprotonation of methanol and initiate transesterification [87]. Zapelini et al. [13] used cetyltrimethyl ammonium bromide (CTAB) and three linear alcohols to prepare different silica. The silica at the basic site is synthesized from cetyltrimethylammonium cations (CTA⁺) in the presence of ethanol, 1-propanol, or 1-butanol to synthesize hybrid silica in the form $\equiv\text{SiO}-\text{CTA}^+$. The catalytic activity is related to the external catalyst site on the outer surface of the particles due to the fact that surfactants block the intermediate pore of the hybrid silica at $\equiv\text{SiO}-\text{CTA}^+$. The samples with larger median diameters of macropores have higher catalytic activity because it is easier to approach the alkaline catalytic sites in these cases. Using *n*-butanol is the best choice for preparing surfactants containing hybrid silica, which has more accessible siloxyl sites.

4.4. Lewis Alkaline Sites Loaded on Hydrotalcite

Layered Double Hydroxide (LDH) is the umbrella term for Hydrotalcite (HT) and Hydrotalcite-Like Compounds (HTLCs) [88]. HTLCs, with their broad specific surface area and heightened surface reactivity, garnering escalating interest in applications in anion exchange, adsorption, and catalytic processes. During the roasting process, HTLCs undergo a dehydration and de-ionization process, creating these mixed oxides through thermal decomposition. This transformation enhances the metal dispersion, specific surface area, and Lewis base characteristics of oxides. HTLCs can easily form mixed metal oxides with high specific surface area, showing Lewis alkaline sites [89,90].

The calcination of hydrotalcite forms mixed oxides, which not only have basic properties but also have attractive properties such as high thermal stability and high surface area. The rehydration treatment of calcined solids can reconstruct the structure of hydrotalcite and completely transform the oxide into the reconstructed hydrotalcite phase, which can improve the solid's thermal stability and significantly increase the catalyst's basicity. Dahdah et al. [91] synthesized Mg-Al hydrotalcite with Mg/Al molar ratio of 3 by co-precipitation method under pH = 9.5 ~ 10 and temperature 60 °C. Then, the solids were calcined at different temperatures (400-600 °C) and rehydrated. The calculated Mg₃Al₂ solids in this study are significantly inefficient regarding transesterification reaction rates. When using the rehydration Mg₃Al₂ catalyst, noticeable improvements were observed. The CO₂-TPD results showed that more robust basic sites were found in the rehydration catalyst compared to calcined competitors. These basic sites play a crucial role in catalyzing transesterification by converting methanol into adsorbed methoxy ions, which attack carbonyl carbon in triglyceride molecules. The basicity of HT materials can be adjusted according to the properties of cations, compensating for ions and activation temperatures. Liu et al. [92] prepared solid basic catalysts by preparing Zn-Al aluminum-aluminum talc at different temperatures. They studied the correlation between the basicity of the solid base and catalytic activity. The basic hydroxyl groups on the surface of zinc aluminum oxide samples are formed through decomposition and absorption of water. Cationic vacancies can be created by incorporating Al³⁺ cations into the ZnO skeleton. For Zn-Al oxides fired at high temperatures, these vacancies may exchange with Zn²⁺ cations on the surface, creating surface-isolated O²⁻ anions. Mⁿ⁺-O²⁻ paired and isolated O²⁻ anions are the primary basic sites. The SBA-15 porous structure is a frequently employed scaffold for crafting solid catalysts, renowned for its customizable structural attributes that facilitate distinctive characteristics. Its orderly architecture, robust hydrothermal endurance, expansive surface area, volume, and well-regulated pore size distribution, positions it a superior candidate for dispersing metal active centers [93]. The SBA-15 supported catalyst, with its high specific surface area, large porosity, and a regular channel structure. The SBA-15 catalyst has been successfully used in biofuels, such as vegetable oil hydrogenation, hinting at its promising future applications in the field of energy [94]. Marimuthu Prabu et al. prepared catalytic active Mg / Al / Zn-HT (HT / SBA-15 nanocomposites) doped with SBA-15. The origin of weak and strong basic sites is attributed to OH⁻ and O²⁻ respectively, which can be called Brønsted and Lewis basic sites.

4.5. Alkaline Metal Based Nanomaterials

Mesoporous nanomaterials have made significant progress and are widely used in biomedicine, petrochemical industry, and catalysis. Nanomaterials can be prepared with various properties and sizes through different synthesis methods [95]. Nanocatalysts have attracted particular attention to biodiesel production because nanoparticles have higher catalytic activity due to their smaller size and uniform dispersion ability [96]. Metal oxide-based catalysts play a crucial role in transesterification catalysis. The key to their catalytic effect lies in the metal elements that bring an alkaline sites. Nanocatalyst carriers can address critical issues such as the leaching of active metal materials into products and their reusability [97,98]. Silva et al. [99] have conducted extensive research on various carbon nitride-based nanomaterials (CNs). Their findings indicate that these CNs have vital sites facilitating the transesterification process, effectively functioning as alkaline catalysts. The presence of these basic sites can be attributed to the incorporation of metallic elements into the catalysts' composition. Chen et al. [100] have successfully synthesized porous Mg-Al-O composite nanoparticles through an aerosol-assisted process. Adding Al_2O_3 to the composite structure significantly enhances the availability of catalytic sites within the nanomaterial framework. Compared to the direct solid-phase thermal decomposition precursor method, the number of sites obtained by the aerosol-based method is significantly increased due to an increase in the specific surface area of MgO dispersion.

5. Lewis Acid-Base Bifunctional Catalyst

Lewis acid/base catalysts have unique characteristics. Over the years, researchers have been working to overcome the catalyst's limitations to produce biodiesel with significant economic benefits. For instance, due to the issue of soap formation in the production of biodiesel with alkaline catalysts and high FFAs raw materials, the reaction conditions for acidic catalysts require higher temperatures and high FFAs interference in-situ transesterification of vegetable oils affects catalytic efficiency, so a new catalyst is needed to promote both FFAs esterification and triglyceride transesterification. The basic characteristics of catalysts containing double Lewis acid-base sites include simultaneous esterification and transesterification ability. They can be modified according to FFAs in different biodiesel feedstocks to achieve the goal of high efficiency and low cost.

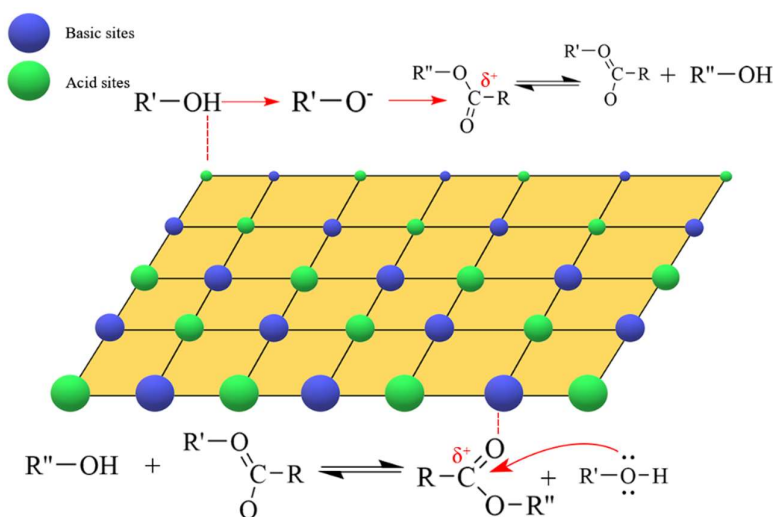


Figure 4. Transesterification of biodiesel at Lewis acid site and basic site.

5.1. Metal Oxide Catalysts containing Lewis Acid-Base Sites

CaO has been extensively studied as a catalyst in t biodiesel production due to its high basicity, biocompatibility, and friendliness to the environment. This metal oxide catalyst can be obtained from natural limestone. CaO reacts with CO_2 and H_2O in the air to form CaCO_3 and Ca(OH)_2 , respectively,

which reduces the activity of the catalyst. Impregnating NiO in CaO can enhance the stability of the catalyst and prepare catalysts with acid-base dual functional sites. NiO stabilizes CaO by inhibiting the reaction of CaO with CO₂ and H₂O to form calcite and Ca(OH)₂ [101]. The acid-base catalyst with an acid-base function was prepared by impregnating the CaO catalyst with NiO. The results show that NiO can catalyze the esterification of fatty acids to methyl ester. Due to the low surface area of CaO, the increase in calcination temperature will increase the alkalinity but will reduce the surface area, loading a bifunctional acid-base nano-catalyst through acid modification, increasing pore volume and specific surface area, adding acid-base sites, improving biodiesel bifunctional performance, to increase the output of biodiesel. have successfully developed a novel class of bifunctional nanocatalysts, comprising CaO and ZrO₂, which have been used to synthesize biodiesel through concurrent esterification and transesterification processes. This innovative approach has produced remarkable results, with the nanocatalyst achieving an exceptional conversion rate of 99% for triglycerides and a significant conversion rate of 73.4% for FFAs [102]. Lanthanum has a unique electronic structure, which is used to receive and lose electrons, so it has dual characteristics of acid and base. FFA interferes with the alkali catalyst, and adding lanthanum enhances transesterification's catalytic ability under high FFA [103]. Lin et al. prepared a Halloysite nanotube functionalized with La-Ca bimetallic oxides as a novel transesterification catalyst. FFA in the reaction system was easy to attack calcium sites, where lanthanum was protected to catalyze the transesterification of triglycerides. The incorporation of lanthanum promoted the adsorption of methanol, promoting transesterification [104]. Lee et al. prepared a bifunctional acid-based CaO-La₂O₃ catalyst. The co-precipitation of La and Ca promoted the dispersion of CaO, increasing the acid and basic sites on the surface. That is to say, the unique synergism between acid-base sites from Ca-O-La, Ca-O-Ca-O, and La-O-La-O bonds can carry out esterification-transesterification at the same time [105]. Vanadium-based catalysts contain Lewis acid and Brønsted acid sites, which play a crucial role in many catalytic processes [106,107]. V₂O₅ is a promising metal oxide that can be used to develop bifunctional catalysts with CaO. Mulyatun et al. studied several kinds of over-doped V₂O₅ to develop acid-base bifunctional group CaO-based catalysts. V₂O₅ can provide Lewis and Brønsted acid sites for acid-base heterogeneous catalyst systems based on CaO. The TPD-NH₃ analysis results show that the V₂O₅-CaO catalyst has more acid sites and the most robust acid strength, which is especially beneficial for catalytic esterification. V₂O₅ contributes Lewis and Brønsted acidity, of which Brønsted acid is responsible for catalytic transesterification. Lewis acids help accelerate the esterification reaction, and the CaO component acts as a Lewis base site to activate the transformation of triglycerides to FAME [108]. Because CaO is the most common heterogeneous alkaline catalyst, combining CaO with other metal oxides (such as ZnO and MgO) [109] can enhance the stability of CaO base catalysts. Some studies have synthesized new heterogeneous catalysts with acidic and basic sites by loading binary metal oxides on CaO. Tungsten-molybdenum-based catalysts have acid-base bifunctional ability. The impregnation of W-Mo catalyst into powdered CaO, Ca-O provides a suitable alkaline site for the conversion of triglycerides to FAME, while W³⁺ and Mo⁶⁺ are considered to be acidic active centers and can esterify a small amount of free fatty acids. Compared to other metal-supported CaO catalysts, bimetallic oxides also have a higher specific surface area, due to the high specific surface area contribution from MoO₃ and WO₃ [110].

5.2. Heteropoly Acid Catalysts with Acid-Base Bifunctional Groups

Boric acid-based catalysts have high Brønsted acidity. Boric acid-based catalysts with metal ions (such as H₃BW₁₁TiO₄₀) produce Lewis acid sites as a synergistic catalyst for esterification [111,112]. Wang et al. successfully prepared a series of new acid-base dual-functional metal boron catalysts using a sol-gel method. Under optimal reaction conditions, the catalysts have high acidity and basic sites. *Jatropha jatropha* oil can be obtained from one pot. The high biodiesel yield is 96.0% [113]. Heteropoly acid (HPAs), especially 12-tungstophosphoric acid (H₃PW₁₂O₄₀, HPW), with a Keggin structure, is recognized as an economical and environmentally friendly heterogeneous acid catalyst due to its good thermal stability, low corrosion, and high acid strength. Cobalt-based zeolite imidazolium skeleton (ZIF-67) has strong Lewis acid-base active sites due to its special Co-N

coordination, which can achieve synergistic catalysis with HPW. Cheng et al. synthesized a new bifunctional heterogeneous catalyst between HPW and ZIF-67, which can effectively catalyze the conversion of triglycerides in microalgae to biodiesel. The terminal W=O group at HPW interacts with the N-terminal of ZIF-67 through a covalent W-O-N bond. The recyclability of the catalyst is enhanced. The released synergistic unsaturated Co cations and N-terminal enhanced the Lewis acid-base properties of the catalyst. They promoted the conversion of microalgae lipids to fatty acid methyl esters, and the catalytic conversion was as high as 98.5% [114]. Lee et al. fabricated a series of triazole heteropolyacid nanocomposites utilizing 1,2,4-triazole and 12-tungstophosphoric acid (PWA) as precursors, employing a precipitation method. These nanocomposites were subsequently applied in the transesterification of rapeseed oil. The optimized formulation of triazole-PWA nanocomposites exhibited commendable structural stability, an expansive surface area, dual functionality, moderate acidity, and pronounced alkalinity. The authors conducted a comparative analysis of the catalytic conversion efficiency between the composite catalyst and its components, triazole, and PWA. The results indicated that the composite catalyst outperformed its constituent elements. This superior catalytic performance is hypothesized to stem from the synergistic effect of bifunctional catalysis, where both acidic and alkaline sites are concurrently enhanced [115].

5.3. Sulfated Solid Acid-Base Amphoteric Catalyst

Solid acid catalysts offer a significant advantage in biodiesel production by eliminating the need for a washing process, simplifying the overall procedure. Their ease of separation from the reaction medium facilitates recovery and reuse and minimizes the risk of acid-induced corrosion and environmental pollution. The versatility of solid acid catalysts is further enhanced by the variety of methods available for their synthesis, with sulfonation being a prominent technique. By meticulously controlling the sulfonation parameters, such as duration, temperature, and the solid-liquid ratio, it is possible to tailor the catalyst's acidity and the number of active sites, thereby enabling the straightforward preparation of catalysts that meet specific requirements with ease [116]. The sulfonic acid group introduction method generally chooses the contact between concentrated H_2SO_4 and carbon to introduce a single bond SO_3H group. The relationship between the catalytic yield of FAME and the concentration of the single bond SO_3H group has been proved. The yield of FAME increases with the increase in the sulfonic group content on the catalyst's surface, which is related to the way of introducing single bond SO_3H groups [117,118]. Sulfation is also suitable for loading other catalysts to form more acid sites and higher acidity to catalyze the transesterification of triglycerides under high FFA, such as those supported on metal oxides [119]. Because the solid acid catalyst requires a high catalyst loading and the reaction time is extended, try to load the sulfonic acid group to the basic metal oxide. The $\text{MgO} / \text{MgSO}_4$ catalyst can carry out transesterification and esterification at the same time, and the catalyst has a high sulfur content of 13.65%. This helps to make it suitable for the high acidity of the esterification step [120]. Shobhana-Gnanaserkhar et al. added alkaline metal oxide CeO_2 , CeO_2 to sulfated activated carbon as an alkaline accelerator to adsorb a large number of sulfur ions to form strong acid sites to achieve simultaneous esterification and transesterification [121]. The high performance of the catalyst containing Ce is due to its high surface area, total alkalinity, and alkali strength. High catalytic activity is also attributed to the large pore size in the catalyst, which makes the diffusion of FFA and triglycerides more significant, so they can react with CeO_2 and Ce_2O_3 in the pores of the catalyst.

5.4. Magnetic Functionalized Double Lewis Acid-Base Sites

Compared to other metals, iron has many advantages, such as low cost, non-toxicity, and environmental protection. However, magnetic particles often gather into large clusters, which hinders the good dispersion of magnetic catalysts in the reaction mixture and reduces the catalyst's recovery efficiency. Magnetic particles encapsulated on the catalyst carrier can create a magnetic multi-functional catalyst carrier, which is an effective way to enhance its chemical stability and prevent aggregation [122]. Some studies have shown that the catalytic effect of doping Fe_3O_4 magnetic nanoparticles on the transesterification catalyst is better than that of the original catalyst, and it is

easy to separate and reduce the catalyst leaching into the mixture. Nurul et al. mixed Fe_3O_4 particles into the zeolite-supported CaO catalyst, the catalyst can effectively transesterification the waste oil with high FFA content, resulting in a large amount of biodiesel. The catalyst has ferromagnetic properties, and the saturation magnetization of 31.759 emu/g makes the separation much easier after the reaction [123]. The CaO-zeolite/ Fe_3O_4 catalyst is both alkaline and acidic, it is suitable for transesterification of raw materials with high FFA content.

Fe_2O_3 catalyst has been used of biodiesel production and as a substitute for acid-base catalyst in transesterification, which makes the biodiesel production process more cost-effective. Because its low toxic nanoparticles can be used to immobilize biological enzymes, they have good adaptability and adjustability under different technological processes [124,125]. The compound Fe_2O_3 is known to enhance the presence of strong acid sites, which are particularly effective for the esterification of FFAs in biodiesel production. Acting as a Lewis acid, it facilitates the adsorption of carboxyl groups, thereby improving the conversion of waste cooking oil into biodiesel. Zahra Mansoorsamaei et al. have developed a novel biochar-supported $\text{Fe}_2\text{O}_3/\text{Fe}_2\text{K}_6\text{O}_5$ catalyst. This catalyst demonstrated significant magnetization values of 2.098 and 5.906 emu/g under a magnetic field of 14000 Oe, indicating its potential for facile recovery using an external magnetic field [126]. The CaO discussed in the previous article has the advantages of an alkaline active site, easy availability, wide source, low cost, and highly catalytic activity, and is also widely used in the synthesis of biodiesel. However, under transesterification, a small amount of soluble matter will be leached from the CaO catalyst [127]. Although Fe_2O_3 has a specific enhancement and stability effect, it is still insufficient. Doping different metal elements in CaO can enhance its structural stability. Xia et al. prepared Co-doped Fe_2O_3 -CaO nanocatalysts. Co was doped into Fe_2O_3 lattice to transform α - Fe_2O_3 crystals into γ - Fe_2O_3 crystals. The catalyst has a stronger magnetic separation strength. Acid-base bifunctional catalysts can effectively esterify FFAs and react with methanol, providing a synergistic acid-base catalytic transesterification effect for biodiesel production [128]. Fe_2O_4 has a high application value in nanomagnetic materials. The magnetic hysteresis loop shows that Fe_2O_4 nanocomposites are ferrimagnetic, and nano-catalyst carriers can enhance the strength of basic sites in them [129,130]. Alkaline oxide ZnFe_2O_4 carried out a synergistic catalytic process by esterification of FFA at the acidic site and transesterifying triglyceride at the alkaline site. Wang et al. studied the synthesis of a magnetic acid-base amphoteric nanoparticle catalyst $\text{Zn}_8\text{@Fe-C400}$. The yield of jatropha curcas biodiesel reached 100.0%. The yield of biodiesel was more than 94.3% after 10 cycles. No significant macroscopic saponification was observed [131].

Co-MOF materials include several strong acid-base sites, and Co pyrolysis forms Co nanoparticles that are partially oxidized to Co_3O_4 . This cobalt oxide gives the catalyst a strong magnetism, and the catalyst can be magnetically separated from the mixture and reused. Guo et al. synthesized bifunctional magnetic acid-base catalysts with different Co and N coordination through the thermal decomposition of ZIF-67 at high temperatures in minutes. The acid-base site allows its FAME conversion rate to reach 96%. [132].

6. Conclusion

Biodiesel is still a sustainable and clean energy under development, but its high cost prevents biodiesel from being widely used. Because biodiesel uses agricultural waste with high FFAs, grain, waste cooking oil, and so on, there are still obstacles in the transesterification process. Fortunately, different from the traditional acid or base catalyzed transesterification, the catalysts suitable for catalytic biodiesel under high FFA conditions are constantly being studied and found, providing a green, efficient, and economical way to produce biodiesel. In this paper, the progress of Lewis acidic and/or alkaline catalysts for transesterification of biodiesel is reviewed, and the importance of the Lewis site in improving catalytic activity is emphasized. This paper starts with the Lewis acid catalyst, Lewis basic catalyst, and Lewis acid-base double site catalyst. The catalyst forms include metal oxides, heterogeneous catalysts supported on zeolites, multi-walled carbon nanotubes, ionic liquids, and eutectic solvents. The role of catalysts containing the Lewis site in the transesterification of biodiesel was reviewed. Traditional Lewis acids have low catalytic activity, but most are easily obtainable and

inexpensive. Adding co-solvents when using these catalysts improves the conversion efficiency of transesterification.

Additionally, we discovered some particular Lewis acids with flocculation functions, which will benefit both the upstream and downstream processes of biodiesel production. Compared to directly using metal chlorides as Lewis acid catalysts, immobilizing catalysts is a more popular trend. The immobilized Lewis acid catalysts will help to reduce the formation of more harmful pollutants. Metal oxides are equipped with Lewis acid sites, or more advanced inorganic carriers such as POMs and CNTs are selected, which significantly enhance the acid strength of the catalyst and the number of Lewis acid sites. ILs and DES are more conducive to the recovery of catalysts and maintaining the activity of homogeneous catalysts. They form a strong force through the electrostatic force between ion pairs, the van der Waals force, and the hydrogen bond between HBD and HBA, which affects the solubility, viscosity, and conductivity of the reaction medium and improves the catalytic activity. Basic catalysts are commonly used catalysts in the production of biodiesel. The article mainly focuses on the pollution and complex operations caused by the exchange of traditional basic catalysts. New catalysts are introduced including alkali metals, alkaline earth metals, silicon oxide anions, Al_2O_3 , SiO_2 , alkali metal-doped hydrotalcite, and alkali metal nanomaterials. These catalysts overcome the shortcomings of traditional alkaline catalyst wastewater and difficult recovery. The Lewis acid-base bifunctional catalyst is a research integration of previous Lewis acid/basic catalysts, hoping to achieve higher efficiency and multifunctional catalysts by developing a catalyst with dual sites. The acidic and basic sites in the composite catalyst bring higher catalytic efficiency and reduce the interference of FFAs on ester exchange. The introduced catalyst loading sites increase the contact area between the catalyst and the reactant. The magnetic catalyst is more convenient for recycling. Many advantages make studying catalysts containing Lewis acidic basic sites more valuable.

Author Contributions: Writing (original draft) Z.Z. (Zhuangzhuang Zhang); resources and project administration, P.M.; visualization, supervision, formal analysis, X.L.; Z.Z. and H.L. All authors have read and agreed to the published version of the manuscript.

Funding: The authors thank the financial support from the High-efficiency and High-value Utilization of Biomass Resources Innovation Team of Guizhou Provincial Higher Education Institution (Qianjiaoji [2023]082), the Program for Natural Science Research in Guizhou Education Department QJJ [2023]024, and the Key Laboratory for Critical Degradation Technologies of Pesticide Residues in Superior Agricultural Products in Guizhou Ecological Environment (QJHKY [2018]005).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Tien Thanh, N.; Mostapha, M.; Lam, M. K.; Ishak, S.; Kanna Dasan, Y.; Lim, J. W.; Tan, I. S.; Lau, S. Y.; Chin, B. L. F.; Hadibarata, T., Fundamental understanding of in-situ transesterification of microalgae biomass to biodiesel: A critical review. *Energy Conversion and Management* **2022**, 270, 116212.
2. Park, J.; Kim, B.; Lee, J. W., In-situ transesterification of wet spent coffee grounds for sustainable biodiesel production. *Bioresource Technology* **2016**, 221, 55-60.
3. Kadir, W. N. A.; Lam, M. K.; Uemura, Y.; Lim, J. W.; Lee, K. T., Harvesting and pre-treatment of microalgae cultivated in wastewater for biodiesel production: A review. *Energy Conversion and Management* **2018**, 171, 1416-1429.
4. Tuntiwiwattanapun, N.; Tongcumpou, C., Sequential extraction and reactive extraction processing of spent coffee grounds: An alternative approach for pretreatment of biodiesel feedstocks and biodiesel production. *Industrial Crops and Products* **2018**, 117, 359-365.
5. Mat Husin, M. A.; Mohd Yasin, N. H.; Takriff, M. S.; Jamar, N. H., A review on pretreatment methods for lipid extraction from microalgae biomass. *Preparative Biochemistry & Biotechnology* **2024**, 54, 159-174.
6. Bauer, G.; Lima, S.; Chenevard, J.; Sugnaux, M.; Fischer, F., Biodiesel via in Situ Wet Microalgae Biotransformation: Zwitter-Type Ionic Liquid Supported Extraction and Transesterification. *ACS Sustainable Chemistry & Engineering* **2017**, 5, 1931-1937.
7. Chiang, C.-L.; Lin, K.-S.; Shu, C.-W.; Wu, J. C.-S.; Wu, K. C.-W.; Huang, Y.-T., Enhancement of biodiesel production via sequential esterification/transesterification over solid superacidic and superbasic catalysts. *Catalysis Today* **2017**, 348, 257-269.

8. Jin, B.; Duan, P.; Xu, Y.; Wang, B.; Wang, F.; Zhang, L., Lewis acid-catalyzed in situ transesterification/esterification of microalgae in supercritical ethanol. *Bioresource Technology* **2014**, 162, 341-349.
9. Encinar, J. M.; Pardal, A.; Sánchez, N.; Nogales, S. Biodiesel by Transesterification of Rapeseed Oil Using Ultrasound: A Kinetic Study of Base-Catalysed Reactions Energies, **2018**.
10. Fadhil, A. B.; Al-Tikrity, E. T. B.; Khalaf, A. M., Transesterification of non-edible oils over potassium acetate impregnated CaO solid base catalyst. *Fuel* **2018**, 234, 81-93.
11. Yang, X.-X.; Wang, Y.-T.; Yang, Y.-T.; Feng, E.-Z.; Luo, J.; Zhang, F.; Yang, W.-J.; Bao, G.-R., Catalytic transesterification to biodiesel at room temperature over several solid bases. *Energy Conversion and Management* **2018**, 164, 112-121.
12. Denmark, S. E.; Beutner, G. L., Lewis base catalysis in organic synthesis. *Angew Chem Int Ed Engl* **2008**, 47, 1560-638.
13. Zapelini, I. W.; Silva, L. L.; Cardoso, D., The role of alcohols on the accessibility of basic $\equiv\text{SiO}^-$ sites in hybrid silicas for catalytic transesterification. *Braz. J. Chem. Eng* **2023**, 41, 409-416.
14. She, Q.; Qiu, M.; Li, K.; Liu, J.; Zhou, C., Acidic and basic sites on the surface of sodium montmorillonite active for catalytic transesterification of glycerol to glycerol carbonate. *Applied Clay Science* **2023**, 238, 106916.
15. Eid, J. G.; de Paula, G. M.; Cardoso, D., Heterogeneous transesterification catalyzed by silicas containing basic sites. *Molecular Catalysis* **2022**, 531, 112631.
16. Abdelgaid, M.; Mpourmpakis, G., Structure–Activity Relationships in Lewis Acid–Base Heterogeneous Catalysis. *ACS Catalysis* **2022**, 12, 4268-4289.
17. Xia, Y.; Chen, L.; Liang, R.; Liu, X.; Yan, G.; Zhu, S.; Wang, X., Bifunctional Lewis acid-base nanocatalysts with dual active sites for strengthened coupling of alcohol conversion and H_2 evolution. *International Journal of Hydrogen Energy* **2024**, 51, 1598-1607.
18. Munyentwali, A.; Li, H.; Yang, Q., Review of advances in bifunctional solid acid/base catalysts for sustainable biodiesel production. *Applied Catalysis A: General* **2022**, 633, 118525.
19. Vicente, G.; Carrero, A.; Rodríguez, R.; del Peso, G. L., Heterogeneous-catalysed direct transformation of microalga biomass into Biodiesel-Grade FAMES. *Fuel* **2017**, 200, 590-598.
20. Bouaid, A.; Vázquez, R.; Martínez, M.; Aracil, J., Effect of free fatty acids contents on biodiesel quality. Pilot plant studies. *Fuel* **2016**, 174, 54-62.
21. Supeno, M.; Sihotang, J. P.; Panjaitan, Y. V.; Damanik, D. S. Y.; Tarigan, J. B.; Sitepu, E. K., Room temperature esterification of high-free fatty acid feedstock into biodiesel. *RSC Advances* **2023**, 13, 33107-33113.
22. Manikandan, G.; Kanna, P. R.; Taler, D.; Sobota, T. Review of Waste Cooking Oil (WCO) as a Feedstock for Biofuel—Indian Perspective Energies, **2023**.
23. Yu, H.; Niu, S.; Lu, C.; Li, J.; Yang, Y., Preparation and esterification performance of sulfonated coal-based heterogeneous acid catalyst for methyl oleate production. *Energy Conversion and Management* **2016**, 126, 488-496.
24. Marchetti, J. M.; Miguel, V. U.; Errazu, A. F., Heterogeneous esterification of oil with high amount of free fatty acids. *Fuel* **2007**, 86, 906-910.
25. Ganesan, S.; Nadarajah, S.; Chee, X. Y.; Khairuddean, M.; Teh, G. B., Esterification of free fatty acids using ammonium ferric sulphate-calcium silicate as a heterogeneous catalyst. *Renewable Energy* **2020**, 153, 1406-1417.
26. Ahmad, A. F.; Zulkurnain, N.; Rosid, S. J. M.; Azid, A.; Endut, A.; Toemen, S.; Ismail, S.; Abdullah, W. N. W.; Aziz, S. M.; Yusoff, N. M.; Rosid, S. M.; Nasir, N. A., Catalytic Transesterification of Coconut Oil in Biodiesel Production: A Review. *Catalysis Surveys from Asia* **2022**, 26, 129-143.
27. Encinar, J. M.; González, J. F.; Martínez, G.; Nogales-Delgado, S. Transesterification of Soybean Oil through Different Homogeneous Catalysts: Kinetic Study Catalysts [Online], **2022**.
28. Johnson, M. B.; Wen, Z., Production of Biodiesel Fuel from the Microalga *Schizochytrium limacinum* by Direct Transesterification of Algal Biomass. *Energy & Fuels* **2009**, 23, 5179-5183.
29. Tiwari, P.; Garg, S., Study of reversible kinetic models for alkali-catalyzed *Jatropha curcas* transesterification. *Biomass Conversion and Biorefinery* **2016**, 6, 61-70.
30. Liu, Y.; Lotero, E.; Goodwin, J. G.; Lu, C., Transesterification of triacetin using solid Brønsted bases. *Journal of Catalysis* **2007**, 246, 428-433.
31. Georgogianni, K. G.; Katsoulidis, A. K.; Pomonis, P. J.; Manos, G.; Kontominas, M. G., Transesterification of rapeseed oil for the production of biodiesel using homogeneous and heterogeneous catalysis. *Fuel Processing Technology* **2009**, 90, 1016-1022.
32. Stojković, I. J.; Stamenković, O. S.; Povrenović, D. S.; Veljković, V. B., Purification technologies for crude biodiesel obtained by alkali-catalyzed transesterification. *Renewable and Sustainable Energy Reviews* **2014**, 32, 1-15.
33. Liu, X.; Piao, X.; Wang, Y.; Zhu, S.; He, H., Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol. *Fuel* **2008**, 87, 1076-1082.

34. Zhao, Z.; Wu, W.; Jia, L.; Guo, X., Sodium phosphate solid base catalysts for production of novel biodiesel by transesterification reaction. *RSC Advances* **2023**, 13, 26700-26708.
35. Kouider Elouahed, S.; Asikin-Mijan, N.; Alsultan G, A.; Kaddour, O.; Yusop, M. R.; Mimoun, H.; Samidin, S.; Mansir, N.; Taufiq-Yap, Y. H., Optimization of the activity of Mo₇-Zn₃/CaO catalyst in the transesterification of waste cooking oil into sustainable biodiesel via response surface methodology. *Energy Conversion and Management* **2024**, 303, 118185.
36. Xie, W.; Zhao, L., Production of biodiesel by transesterification of soybean oil using calcium supported tin oxides as heterogeneous catalysts. *Energy Conversion and Management* **2013**, 76, 55-62.
37. Ma, X.; Liu, F.; Helian, Y.; Li, C.; Wu, Z.; Li, H.; Chu, H.; Wang, Y.; Wang, Y.; Lu, W.; Guo, M.; Yu, M.; Zhou, S., Current application of MOFs based heterogeneous catalysts in catalyzing transesterification/esterification for biodiesel production: A review. *Energy Conversion and Management* **2021**, 229, 113760.
38. Shahidul Islam, M.; Robin Hart, C.; Casadonte, D., Ultrasound-assisted solid Lewis acid-catalyzed transesterification of Lesquerella fendleri oil for biodiesel synthesis. *Ultrasonics Sonochemistry* **2022**, 88, 106082.
39. Casas, A.; Ramos, M. J.; Rodríguez, J. F.; Pérez, Á., Tin compounds as Lewis acid catalysts for esterification and transesterification of acid vegetable oils. *Fuel Processing Technology* **2013**, 106, 321-325.
40. Guan, Q.; Shang, H.; Liu, J.; Gu, J.; Li, B.; Miao, R.; Chen, Q.; Ning, P., Biodiesel from transesterification at low temperature by AlCl₃ catalysis in ethanol and carbon dioxide as cosolvent: Process, mechanism and application. *Applied Energy* **2016**, 164, 380-386.
41. Soriano, N. U.; Venditti, R.; Argyropoulos, D. S., Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification. *Fuel* **2009**, 88, 560-565.
42. Chin, S. Y.; Ahmad, A. L.; Mohamed, A. R.; Bhatia, S., Characterization and activity of zinc acetate complex supported over functionalized silica as a catalyst for the production of isopropyl palmitate. *Applied Catalysis A: General* **2006**, 297, 8-17.
43. Di Serio, M.; Tesser, R.; Dimiccoli, M.; Cammarota, F.; Nastasi, M.; Santacesaria, E., Synthesis of biodiesel via homogeneous Lewis acid catalyst. *Journal of Molecular Catalysis A: Chemical* **2005**, 239, 111-115.
44. Reinoso, D. M.; Damiani, D. E.; Tonetto, G. M., Zinc carboxylic salts used as catalyst in the biodiesel synthesis by esterification and transesterification: Study of the stability in the reaction medium. *Applied Catalysis A: General* **2012**, 449, 88-95.
45. Kolet, M.; Atrash, M.; Molina, K.; Zerbib, D.; Albo, Y.; Nakonechny, F.; Nisnevitch, M. Sol-Gel Entrapped Lewis Acids as Catalysts for Biodiesel Production. *Molecules* **2020**, 25, 5936.
46. Mello, V. M.; Pousa, G. P. A. G.; Pereira, M. S. C.; Dias, I. M.; Suarez, P. A. Z., Metal oxides as heterogeneous catalysts for esterification of fatty acids obtained from soybean oil. *Fuel Processing Technology* **2011**, 92, 53-57.
47. Raia, R. Z.; da Silva, L. S.; Marcucci, S. M. P.; Arroyo, P. A., Biodiesel production from Jatropha curcas L. oil by simultaneous esterification and transesterification using sulphated zirconia. *Catalysis Today* **2017**, 289, 105-114.
48. Du, Y.; Liu, S.; Ji, Y.; Zhang, Y.; Wei, S.; Liu, F.; Xiao, F.-S., Synthesis of Sulfated Silica-Doped Tin Oxides and Their High Activities in Transesterification. *Catalysis Letters* **2008**, 124, 133-138.
49. Li, D.; Feng, W.; Chen, C.; Chen, S.; Fan, G.; Liao, S.; Wu, G.; Wang, Z., Transesterification of Litsea cubeba kernel oil to biodiesel over zinc supported on zirconia heterogeneous catalysts. *Renewable Energy* **2021**, 177, 13-22.
50. Hechelski, M.; Ghinet, A.; Louvel, B.; Dufrénoy, P.; Rigo, B.; Daïch, A.; Waterlot, C., From Conventional Lewis Acids to Heterogeneous Montmorillonite K10: Eco-Friendly Plant-Based Catalysts Used as Green Lewis Acids. *ChemSusChem* **2018**, 11, 1249-1277.
51. Shestakova, P.; Popova, M.; Szegedi, Á.; Lazarova, H.; Nga Luong, T. K.; Trendafilova, I.; Mihály, J.; Parac-Vogt, T. N., Hybrid catalyst with combined Lewis and Brønsted acidity based on ZrIV substituted polyoxometalate grafted on mesoporous MCM-41 silica for esterification of renewable levulinic acid. *Microporous and Mesoporous Materials* **2021**, 323, 111203.
52. Aziz, M. A. A.; Puad, K.; Triwahyono, S.; Jalil, A. A.; Khayoon, M. S.; Atabani, A. E.; Ramli, Z.; Majid, Z. A.; Prasetyoko, D.; Hartanto, D., Transesterification of croton megalocarpus oil to biodiesel over WO₃ supported on silica mesoporous-macroparticles catalyst. *Chemical Engineering Journal* **2017**, 316, 882-892.
53. Duan, Y.; Ding, R.; Shi, Y.; Fang, X.; Hu, H.; Yang, M.; Wu, Y. Synthesis of Renewable Diesel Range Alkanes by Hydrodeoxygenation of Palmitic Acid over 5% Ni/CNTs under Mild Conditions. *Catalysts* **2017**, 7, 81.
54. Shu, Q.; Zou, W.; He, J.; Lesmana, H.; Zhang, C.; Zou, L.; Wang, Y., Preparation of the F-SO₄²⁻/MWCNTs catalyst and kinetic studies of the biodiesel production via esterification reaction of oleic acid and methanol. *Renewable Energy* **2019**, 135, 836-845.
55. Shu, Q.; Tang, G.; Liu, F.; Zou, W.; He, J.; Zhang, C.; Zou, L., Study on the preparation, characterization of a novel solid Lewis acid Al³⁺-SO₄²⁻/MWCNTs catalyst and its catalytic performance for the synthesis of biodiesel via esterification reaction of oleic acid and methanol. *Fuel* **2017**, 209, 290-298.

56. Ibrahim, M. L.; Nik Abdul Khalil, N. N. A.; Islam, A.; Rashid, U.; Ibrahim, S. F.; Sinar Mashuri, S. I.; Taufiq-Yap, Y. H., Preparation of Na₂O supported CNTs nanocatalyst for efficient biodiesel production from waste-oil. *Energy Conversion and Management* **2020**, 205, 112445.
57. Hasan, Z.; Jun, J. W.; Jhung, S. H., Sulfonic acid-functionalized MIL-101(Cr): An efficient catalyst for esterification of oleic acid and vapor-phase dehydration of butanol. *Chemical Engineering Journal* **2015**, 278, 265-271.
58. Guo, J.; Zheng, Y.; Li, Y.; Wen, Z.; Shen, X.; Zhao, Y., Application of functional metal anionic Lewis acid ionic liquids in the alkylation of chlorobenzene/SOCl₂. *RSC Advances* **2023**, 13, 11635-11641.
59. Ullah, Z.; Khan, A. S.; Muhammad, N.; Ullah, R.; Alqahtani, A. S.; Shah, S. N.; Ghanem, O. B.; Bustam, M. A.; Man, Z., A review on ionic liquids as perspective catalysts in transesterification of different feedstock oil into biodiesel. *Journal of Molecular Liquids* **2018**, 266, 673-686.
60. Panchal, B.; Chang, T.; Qin, S.; Sun, Y.; Wang, J.; Bian, K., Optimization of soybean oil transesterification using an ionic liquid and methanol for biodiesel synthesis. *Energy Reports* **2020**, 6, 20-27.
61. Han, X.; Yan, W.; Hung, C.-T.; He, Y.; Wu, P.-H.; Liu, L.-L.; Huang, S.-J.; Liu, S.-B., Transesterification of soybean oil to biodiesel by tin-based Brønsted-Lewis acidic ionic liquid catalysts. *Korean Journal of Chemical Engineering* **2016**, 33, 2063-2072.
62. Xie, W.; Wan, F., Immobilization of polyoxometalate-based sulfonated ionic liquids on UiO-66-2COOH metal-organic frameworks for biodiesel production via one-pot transesterification-esterification of acidic vegetable oils. *Chemical Engineering Journal* **2019**, 365, 40-50.
63. Yu, Y.; Yu, F.; Li, L.; Yuan, B.; Xie, C.; Yu, S., Lewis acidic deep eutectic solvents as catalysts for rosin polymerization. *New Journal of Chemistry* **2023**, 47, 20144-20150.
64. Bai, Y.; Zhang, X.-F.; Wang, Z.; Zheng, T.; Yao, J., Deep eutectic solvent with bifunctional Brønsted-Lewis acids for highly efficient lignocellulose fractionation. *Bioresource Technology* **2022**, 347, 126723.
65. Wang, Z.-K.; Hong, S.; Wen, J.-L.; Ma, C.-Y.; Tang, L.; Jiang, H.; Chen, J.-J.; Li, S.; Shen, X.-J.; Yuan, T.-Q., Lewis Acid-Facilitated Deep Eutectic Solvent (DES) Pretreatment for Producing High-Purity and Antioxidative Lignin. *ACS Sustainable Chemistry & Engineering* **2020**, 8, 1050-1057.
66. Chen, H.; Sun, C.; Hu, Y.; Xia, C.; Sun, F.; Zhang, Z., Reaction characteristics of metal-salt coordinated deep eutectic solvents during lignocellulosic pretreatment. *Journal of Environmental Chemical Engineering* **2023**, 11, 109531.
67. Liu, W.; Wang, F., *p*-Toluenesulfonic Acid-based Deep Eutectic Solvent as Transesterification Catalyst for Biodiesel Production. *Journal of Oleo Science* **2018**, 67, 1163-1169.
68. Potchamyou Ngatcha, A. D.; Zhao, A.; Zhang, S.; Xiong, W.; Sarker, M.; Xu, J.; Alam, M. A., Determination of active sites on the synthesis of novel Lewis acidic deep eutectic solvent catalysts and kinetic studies in microalgal biodiesel production. *RSC Advances* **2023**, 13, 10110-10122.
69. Alam, M. A.; Deng, L.; Ngatcha, A. D. P.; Fouegue, A. D. T.; Wu, J.; Zhang, S.; Zhao, A.; Xiong, W.; Xu, J., Biodiesel production from microalgal biomass by Lewis acidic deep eutectic solvent catalysed direct transesterification. *Industrial Crops and Products* **2023**, 206, 117725.
70. Yang, Z.-J.; Peng, S.-Y.; Wang, H.; Zhang, Z.-Q.; Xu, Y.-P.; Sun, J.; Xu, Z.-N.; Guo, G.-C., Enhanced catalytic activity for CO esterification to dimethyl oxalate via increasing Lewis basic sites in Pd/MgAl-LDO catalyst. *Catalysis Communications* **2023**, 184, 106781.
71. Zhang, S.; He, H.; Sun, F.; Zhao, N.; Du, J.; Pan, Q.; Zhu, G., A novel adenine-based zinc(II) metal-organic framework featuring the Lewis basic sites for heterogeneous catalysis. *Inorganic Chemistry Communications* **2017**, 79, 55-59.
72. Liu, X.; Fan, W.; Zhang, M.; Li, G.; Liu, H.; Sun, D.; Zhao, L.; Zhu, H.; Guo, W., Enhancing light hydrocarbon storage and separation through introducing Lewis basic nitrogen sites within a carboxylate-decorated copper-organic framework. *Materials Chemistry Frontiers* **2018**, 2, 1146-1154.
73. Naganawa, Y.; Abe, H.; Nishiyama, H., Design of bifunctional chiral phenanthroline ligand with Lewis basic site for palladium-catalyzed asymmetric allylic substitution. *Chemical Communications* **2018**, 54, 2674-2677.
74. Hassan, H. M. A.; Alhumaimess, M. S.; Kamel, M. M.; Alsohaimi, I. H.; Aljaddua, H. I.; Aldosari, O. F.; Algamdi, M. S.; Mohamed, R. M. K.; El-Aassar, M. R., Electrospinning NH₂-MIL-101/PAN nanofiber mats: A promising catalyst with Lewis acidic and basic bifunctional sites for organic transformation reactions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2022**, 642, 128659.
75. Zhao, G.; Liu, Y.; Pan, J.; Liu, C.; Hu, Y.; Gao, Z.; Zhuang, X., Flexible nanofibrous membranes of dual metallic metal-organic framework with enhanced Lewis basic sites and high loading mass for efficient CO₂ capture. *Journal of Colloid and Interface Science* **2023**, 651, 200-210.
76. Machorro, J. J.; Lazaro, A. L.; Espejel-Ayala, F.; Coutiño-Gonzalez, E.; Chavarria-Hernandez, J. C.; Godínez, L. A.; Rodríguez-Valadez, F. J. The Roles of the Structure and Basic Sites of Sodium Titanates on Transesterification Reactions to Obtain Biodiesel Catalysts [Online], 2019.
77. Cannilla, C.; Bonura, G.; Arena, F.; Rombi, E.; Frusteri, F., How surface and textural properties affect the behaviour of Mn-based catalysts during transesterification reaction to produce biodiesel. *Catalysis Today* **2012**, 195, 32-43.

78. Lingfeng, C.; Guomin, X.; Bo, X.; Guangyuan, T., Transesterification of Cottonseed Oil to Biodiesel by Using Heterogeneous Solid Basic Catalysts. *Energy & Fuels* **2007**, 21, 3740-3743.
79. Pampararo, G.; Debecker, D. P., Sodium Aluminate-Catalyzed Biodiesel Synthesis. *ACS Sustainable Chemistry & Engineering* **2023**, 11, 10413-10421.
80. Singh, H.; Ali, A., Esterification as well as transesterification of waste oil using potassium imbued tungstophosphoric acid supported graphene oxide as heterogeneous catalyst: Optimization and kinetic modeling. *Renewable Energy* **2023**, 207, 422-435.
81. Tavizón-Pozos, J. A.; Chavez-Esquivel, G.; Suárez-Toriello, V. A.; Santolalla-Vargas, C. E.; Luévano-Rivas, O. A.; Valdés-Martínez, O. U.; Talavera-López, A.; Rodríguez, J. A. State of Art of Alkaline Earth Metal Oxides Catalysts Used in the Transesterification of Oils for Biodiesel Production *Energies* **2021**, 14, 1031.
82. Cabrera-Munguia, D. A.; González, H.; Barreto-Gutiérrez, M.; Gutiérrez-Alejandro, A.; Rico, J. L.; Solís-Casados, D. A., Tuning the Basic Properties of ZnAl Hydrotalcites Modified with Ce Applied to Transesterification of Soybean Oil. *Catalysis Letters* **2020**, 150, 1957-1969.
83. Wang, Z.; Zhou, H.; Liu, Z.; Miao, R.; He, L.; Guan, Q., Walnut-shaped calcium oxide-cancrinite spheres for transesterification of waste frying oil. *Renewable Energy* **2023**, 208, 229-239.
84. Singh, V.; Hameed, B. H.; Sharma, Y. C., Economically viable production of biodiesel from a rural feedstock from eastern India, *P. pinnata* oil using a recyclable laboratory synthesized heterogeneous catalyst. *Energy Conversion and Management* **2016**, 122, 52-62.
85. Wang, J.; Yang, L.; Luo, W.; Yang, G.; Miao, C.; Fu, J.; Xing, S.; Fan, P.; Lv, P.; Wang, Z., Sustainable biodiesel production via transesterification by using recyclable $\text{Ca}_2\text{MgSi}_2\text{O}_7$ catalyst. *Fuel* **2017**, 196, 306-313.
86. Alkimim, I. P.; Silva, L. L.; Cardoso, D., Synthesis of hybrid spherical silicas and application in catalytic transesterification reaction. *Microporous and Mesoporous Materials* **2017**, 254, 37-44.
87. Kubota, Y.; Nishizaki, Y.; Ikeya, H.; Saeki, M.; Hida, T.; Kawazu, S.; Yoshida, M.; Fujii, H.; Sugi, Y., Organic-silicate hybrid catalysts based on various defined structures for Knoevenagel condensation. *Microporous and Mesoporous Materials* **2004**, 70, 135-149.
88. Zhao, S.; Yi, H.; Tang, X.; Kang, D.; Yu, Q.; Gao, F.; Wang, J.; Huang, Y.; Yang, Z., Mechanism of activity enhancement of the Ni based hydrotalcite-derived materials in carbonyl sulfide removal. *Materials Chemistry and Physics* **2018**, 205, 35-43.
89. Álvarez, M. G.; Plíšková, M.; Segarra, A. M.; Medina, F.; Figueras, F., Synthesis of glycerol carbonates by transesterification of glycerol in a continuous system using supported hydrotalcites as catalysts. *Applied Catalysis B: Environmental* **2012**, 113-114, 212-220.
90. Coumans, F. J. A. G.; Mitchell, S.; Schütz, J.; Medlock, J.; Pérez-Ramírez, J., Hydrotalcite-Derived Mixed Oxides for the Synthesis of a Key Vitamin A Intermediate Reducing Waste. *ACS Omega* **2018**, 3, 15293-15301.
91. Dahdah, E.; Estephane, J.; Taleb, Y.; El Khoury, B.; El Nakat, J.; Aouad, S., The role of rehydration in enhancing the basic properties of Mg-Al hydrotalcites for biodiesel production. *Sustainable Chemistry and Pharmacy* **2021**, 22, 100487.
92. Liu, Q.; Wang, B.; Wang, C.; Tian, Z.; Qu, W.; Ma, H.; Xu, R., Basicities and transesterification activities of Zn-Al hydrotalcites-derived solid bases. *Green Chemistry* **2014**, 16, 2604-2613.
93. Sánchez Faba, E. M.; Ferrero, G. O.; Dias, J. M.; Eimer, G. A., Thermo-chemically tuning of active basic sites on nanoarchitected silica for biodiesel production. *Molecular Catalysis* **2020**, 481, 110171.
94. Wang, H.; Yan, S.; Salley, S. O.; Simon Ng, K. Y., Support effects on hydrotreating of soybean oil over NiMo carbide catalyst. *Fuel* **2013**, 111, 81-87.
95. Ryoo, R., Birth of a class of nanomaterial. *Nature* **2019**, 575, 40-41.
96. Davoodbasha, M.; Pugazhendhi, A.; Kim, J.-W.; Lee, S.-Y.; Nooruddin, T., Biodiesel production through transesterification of *Chlorella vulgaris*: Synthesis and characterization of CaO nanocatalyst. *Fuel* **2021**, 300, 121018.
97. Kumari, N.; Aulakh, M. K.; Sareen, S.; Sharma, A.; Sohal, H. S.; Verma, M.; Mehta, S. K.; Mutreja, V., Greener Synthesis of Zirconium-Based Nanocatalyst for Transesterification. *Topics in Catalysis* **2022**, 65, 1811-1820.
98. Al-Abbasi, A.; Almahdi, F.; Almakry, M.; Izriq, R.; Milad, A.; Salim, S.; Najjar, A., BaO as a heterogeneous nanoparticle catalyst in oil transesterification for the production of FAME fuel. *Inorganic Chemistry Communications* **2023**, 158, 111620.
99. Silva, I. F.; Rios, R. D. F.; Savateev, O.; Teixeira, I. F., Carbon Nitride-Based Nanomaterials as a Sustainable Catalyst for Biodiesel Production. *ACS Applied Nano Materials* **2023**, 6, 9718-9727.
100. Chen, Y.-S.; Yang, C.-M.; Nguyen Hoang, T. T.; Tsai, D.-H., Porous magnesia-alumina composite nanoparticle for biodiesel production. *Fuel* **2021**, 285, 119203.
101. Widiarti, N.; Bahruji, H.; Holilah, H.; Ni'mah, Y. L.; Ediati, R.; Santoso, E.; Jalil, A. A.; Hamid, A.; Prasetyoko, D., Upgrading catalytic activity of NiO/CaO/MgO from natural limestone as catalysts for transesterification of coconut oil to biodiesel. *Biomass Conversion and Biorefinery* **2023**, 13, 3001-3015.
102. Ghasemi, I.; Haghighi, M.; Bekhradinassab, E.; Ebrahimi, A., Ultrasound-assisted dispersion of bifunctional CaO-ZrO₂ nanocatalyst over acidified kaolin for production of biodiesel from waste cooking oil. *Renewable Energy* **2024**, 225, 120287.

103. Abdulkareem-Alsultan, G.; Asikin-Mijan, N.; Lee, H. V.; Taufiq-Yap, Y. H., A new route for the synthesis of La-Ca oxide supported on nano activated carbon via vacuum impregnation method for one pot esterification-transesterification reaction. *Chemical Engineering Journal* **2016**, 304, 61-71.
104. Lin, T.; Zhao, S.; Niu, S.; Lyu, Z.; Han, K.; Hu, X., Halloysite nanotube functionalized with La-Ca bimetallic oxides as novel transesterification catalyst for biodiesel production with molecular simulation. *Energy Conversion and Management* **2020**, 220, 113138.
105. Lee, H. V.; Juan, J. C.; Taufiq-Yap, Y. H., Preparation and application of binary acid-base CaO-La₂O₃ catalyst for biodiesel production. *Renewable Energy* **2015**, 74, 124-132.
106. Nuguid, R. J. G.; Ortino-Ghini, L.; Suskevich, V. L.; Yang, J.; Lietti, L.; Kröcher, O.; Ferri, D., Interconversion between Lewis and Brønsted-Lowry acid sites on vanadia-based catalysts. *Physical Chemistry Chemical Physics* **2022**, 24, 4555-4561.
107. Marberger, A.; Ferri, D.; Elsener, M.; Kröcher, O., The Significance of Lewis Acid Sites for the Selective Catalytic Reduction of Nitric Oxide on Vanadium-Based Catalysts. *Angewandte Chemie International Edition* **2016**, 55, 11989-11994.
108. Mulyatun, M.; Prameswari, J.; Istadi, I.; Widayat, W., Synthesis Method Effect on the Catalytic Performance of Acid-Base Bifunctional Catalysts for Converting Low-Quality Waste Cooking Oil to Biodiesel. *Catalysis Letters* **2024**, 154, 4837-4855.
109. Kesica, Z.; Lukic, I.; Zdujic, M.; Liu, H.; Skala, D., Mechanochemically Synthesized CaO ZnO Catalyst For Biodiesel Production. *Procedia Engineering* **2012**, 42, 1169-1178.
110. Mansir, N.; Hwa Teo, S.; Lokman Ibrahim, M.; Yun Hin, T.-Y., Synthesis and application of waste egg shell derived CaO supported W-Mo mixed oxide catalysts for FAME production from waste cooking oil: Effect of stoichiometry. *Energy Conversion and Management* **2017**, 151, 216-226.
111. Yan, S.; Tong, T.; Li, Y.; Khan, S. U.; Zhao, J.; Wang, S.; Wang, X., Production of Biodiesel Through Esterification Reaction Using Choline Exchanging Polytungstoboronic Acids as Temperature-Responsive Catalysts. *Catalysis Surveys from Asia* **2017**, 21, 151-159.
112. Lapis, A. A. M.; de Oliveira, L. F.; Neto, B. A. D.; Dupont, J., Ionic Liquid Supported Acid/Base-Catalyzed Production of Biodiesel. *ChemSusChem* **2008**, 1, 759-762.
113. Wang, A.; Li, H.; Zhang, H.; Pan, H.; Yang, S. Efficient Catalytic Production of Biodiesel with Acid-Base Bifunctional Rod-Like Ca-B Oxides by the Sol-Gel Approach. *Materials*, **2019**, 12, 83.
114. Cheng, J.; Guo, H.; Yang, X.; Mao, Y.; Qian, L.; Zhu, Y.; Yang, W., Phosphotungstic acid-modified zeolite imidazolate framework (ZIF-67) as an acid-base bifunctional heterogeneous catalyst for biodiesel production from microalgal lipids. *Energy Conversion and Management* **2021**, 232, 113872.
115. Lee, G.; Lee, C.; Kim, H.; Jeon, Y.; Shul, Y.-G.; Park, J. Bifunctional 1,2,4-Triazole/12-Tungstophosphoric Acid Composite Nanoparticles for Biodiesel Production. *Nanomaterials* **2022**, 12, 4022.
116. Mansir, N.; Taufiq-Yap, Y. H.; Rashid, U.; Lokman, I. M., Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production: A review. *Energy Conversion and Management* **2017** 141, 171-182.
117. Rechnia-Gorący, P.; Malaika, A.; Kozłowski, M., Acidic activated carbons as catalysts of biodiesel formation. *Diamond and Related Materials* **2018**, 87, 124-133.
118. Rocha, P. D.; Oliveira, L. S.; Franca, A. S., Sulfonated activated carbon from corn cobs as heterogeneous catalysts for biodiesel production using microwave-assisted transesterification. *Renewable Energy* **2019**, 143, 1710-1716.
119. Luo, Y.; Mei, Z.; Liu, N.; Wang, H.; Han, C.; He, S., Synthesis of mesoporous sulfated zirconia nanoparticles with high surface area and their applies for biodiesel production as effective catalysts. *Catalysis Today* **2017**, 298, 99-108.
120. Bora, A. P.; Konda, L. D. N. V. V.; Pasupuleti, S.; Durbha, K. S., Synthesis of MgO/MgSO₄ nanocatalyst by thiourea-nitrate solution combustion for biodiesel production from waste cooking oil. *Renewable Energy* **2022**, 190, 474-486.
121. Shobhana, G.; Asikin-Mijan, N.; Abdulkareem-Alsultan, G.; Sivasangar, S.; Izham, S. M.; Taufiq-Yap, Y. H., Biodiesel production via simultaneous esterification and transesterification of chicken fat oil by mesoporous sulfated Ce supported activated carbon. *Biomass and Bioenergy* **2020**, 141, 105714.
122. Li, H.; Liu, F.; Ma, X.; Cui, P.; Guo, M.; Li, Y.; Gao, Y.; Zhou, S.; Yu, M., An efficient basic heterogeneous catalyst synthesis of magnetic mesoporous Fe@C support SrO for transesterification. *Renewable Energy* **2020**, 149, 816-827.
123. Lani, N. S.; Ngadi, N.; Mohammed Inuwa, I.; Anako Opotu, L.; Zakaria, Z. Y.; Haron, S., A cleaner approach with magnetically assisted reactor setup over CaO-zeolite/Fe₃O₄ catalyst in biodiesel production: Evaluation of catalytic performance, reusability and life cycle assessment studies. *Journal of Cleaner Production* **2023**, 419, 138329.
124. Banerjee, S.; Rout, S.; Banerjee, S.; Atta, A.; Das, D., Fe₂O₃ nanocatalyst aided transesterification for biodiesel production from lipid-intact wet microalgal biomass: A biorefinery approach. *Energy Conversion and Management* **2019**, 195, 844-853.

125. Xie, W.; Zang, X., Covalent immobilization of lipase onto aminopropyl-functionalized hydroxyapatite-encapsulated- γ -Fe₂O₃ nanoparticles: A magnetic biocatalyst for interesterification of soybean oil. *Food Chemistry* **2017**, 227, 397-403.
126. Mansoorsamaei, Z.; Mowla, D.; Esmaeilzadeh, F.; Dashtian, K., Sustainable biodiesel production from waste cooking oil using banana peel biochar-Fe₂O₃/Fe₂K₆O₅ magnetic catalyst. *Fuel* **2024**, 357, 129821.
127. Kouzu, M.; Hidaka, J.-s., Purification to remove leached CaO catalyst from biodiesel with the help of cation-exchange resin. *Fuel* **2013**, 105, 318-324.
128. Xia, S.; Li, J.; Chen, G.; Tao, J.; Li, W.; Zhu, G., Magnetic reusable acid-base bifunctional Co doped Fe₂O₃-CaO nanocatalysts for biodiesel production from soybean oil and waste frying oil. *Renewable Energy* **2022**, 189, 421-434.
129. Kannapiran, N.; Muthusamy, A.; Renganathan, B.; Ganesan, A. R.; Savithiri, S.; Meena, S. S., Magnetic, Dielectric and Ethanol Gas Sensing Properties of Poly(o-phenylenediamine)/(MnNi)Fe₂O₄ Nanocomposites and Quantum Chemical Calculations of (MnNi)Fe₂O₄. *Journal of Inorganic and Organometallic Polymers and Materials* **2022**, 32, 2173-2191.
130. Rahmanivahid, B.; Ajamein, H.; Zakizadeh, T.; Nayeibzadeh, H., Fabrication of super basic BaxMg(1-x)Fe₂O₄ magnetic spinel nanocatalyst toward biodiesel production. *Materials Research Bulletin* **2023**, 165, 112321.
131. Wang, Y.-T.; Fang, Z.; Yang, X.-X.; Yang, Y.-T.; Luo, J.; Xu, K.; Bao, G.-R., One-step production of biodiesel from Jatropha oils with high acid value at low temperature by magnetic acid-base amphoteric nanoparticles. *Chemical Engineering Journal* **2018**, 348, 929-939.
132. Guo, H.; Cheng, J.; Mao, Y.; Qian, L.; Shao, Y.; Yang, W., Fabricating different coordination states of cobalt as magnetic acid-base bifunctional catalyst for biodiesel production from microalgal lipid. *Fuel* **2022**, 322, 124172.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.