

A Review on Heterogeneous Catalysts Containing Basic Active Sites for Biodiesel Production

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ABSTRACT

The production of biodiesel using transesterification has drawn significant scientific interest as a renewable and eco-friendly substitute for petroleum diesel. Among the catalytic systems studied, heterogeneous catalysts with basic active sites have emerged as leading candidates due to their high catalytic activity, ease of separation, and reusability. This review synthesizes findings from 54 studies published between 2015 and 2026, examining the role of basic active sites in the transesterification mechanism across alkaline earth metal oxides, mixed metal oxides, supported catalysts, waste-derived catalysts, hydrotalcites, zeolites, metal-organic frameworks, and nanostructured materials. Catalytic performance is governed largely by surface area, pore structure, and the density, strength, and accessibility of basic active sites. CaO-based catalysts remain the most widely studied, reporting biodiesel yields above 90% under optimized conditions owing to strong basicity and low cost, though they remain susceptible to deactivation via carbonation and hydration. Waste-derived catalysts offer sustainable, low-cost alternatives, while mixed-metal and doped systems show improved stability, retaining activity over multiple reaction cycles depending on catalyst type. Despite these advances, large-scale application remains constrained by feedstock quality, active-species leaching, and catalyst deactivation. Future research should prioritize highly stable, reusable, and cost-effective catalysts with improved basic-site accessibility, alongside standardized reporting of reaction conditions to enable meaningful comparison across studies.

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INTRODUCTION

Global energy demand, diminishing fossil fuel reserves, and mounting environmental concerns have driven sustained research into renewable fuel alternatives. Biodiesel, produced primarily via transesterification of triglycerides with short-chain alcohols, has emerged as a leading substitute for petroleum diesel due to its biodegradability, low toxicity, and reduced emissions relative to conventional diesel (Ogunkunle & Ahmed, 2021).

The choice of catalysts is crucial to the effectiveness of transesterification. Because of their high activity and quick kinetics, homogeneous alkaline catalysts like KOH and NaOH are still frequently used in industry (Bhan *et al.*, 2025). Also, they are intolerant of feedstocks with high free fatty acid content, produce wastewater and soap byproducts, and are challenging to separate and recover (Shende *et al.*, 2019). These restrictions are immediately addressed by heterogeneous catalysts, which provide easier separation, reusability, and less wastewater production (Parangi, 2025). Catalysts with basic active sites, which activate methanol to create reactive methoxide species that attack triglyceride molecules, have garnered special interest within this class. The density, strength, and accessibility of these sites control both reaction rate and biodiesel yield (Miceli *et al.*, 2021).

Alkaline earth metal oxides, mixed metal oxides, supported catalysts, waste-derived catalysts, hydrotalcites, and nanostructured materials are some of the classes of basic heterogeneous catalysts that have been developed and studied. Previous reviews have addressed subsets of this

landscape (e.g., waste-derived catalysts specifically catalysts types broadly: Modern synthesis (Bhan *et al.*, 2025).

Instead of treating catalysts types as distinct categories, this review connects sites level properties (density, strength, accessibility) to catalytic performance, characterization strategy, and deactivation behavior by concentrating on the role of basic active sites as the unifying feature across catalysts classes (Yaghi *et al.*, 2025).

Therefore, this review is structured as follows: The transesterification reaction and biodiesel synthesis are covered in Section 2. The principles of fundamental active sites are examined in Section 3; Major catalysts types are categorized and discussed in Section 4, characterisation methods and catalytic performance are assessed in Section 5, and current issues, deactivation processes, and future research directions for industrially feasible basic heterogeneous catalysts are discussed in the concluding parts.

Biodiesel Production and Transesterification Reaction Overview

Traditionally, biodiesel is made by transesterifying triglycerides (from vegetable oils, animal fats, or waste oils) with a short-chain alcohol, usually methanol, in the presence of a catalysts. The process produces glycerol and fatty acid methyl esters (FAME) as byproducts.

Feedstock Classification

The main categories of biodiesel feedstocks include waste cooking oils, animal fats, edible oils (like soybean, palm, and sunflower), and non-edible oils (such *Jatropha*, castor, and

karanja). Free fatty acid (FFA) concentration, water content, and overall process economics are all impacted by feedstock selection; waste-derived and inedible feedstocks are typically chosen to prevent food versus fuel competition.

Emerging and Alternative Feedstock

Due to their potential to circumvent the land use and food competition issues related to edible oils, a number of new feedstocks are attracting study interest in addition to conventional sources. Although cultivation and lipid extraction expenses continue to be obstacles to commercialization, algal oils derived from microalgae and macroalgae offer significant lipid yields per unit area and do not require arable land. Another interesting approach is the

production of microbial oils by oleaginous yeasts and fungi, which can accumulate significant intracellular lipid content when grown on inexpensive carbon sources, such as industrial and agricultural waste streams. Because of their capacity to transform organic waste into useful lipid feedstock and their quick biomass accumulation, insect derived lipids especially those from black soldier fly larvae have also attracted attention. In order to increase feedstock consistency and yield, genetically modified oilseed crops with changed fatty acid profiles or increased oil content are also being investigated. Even while scaling up each of these sources has unique technical and financial obstacles, taken as a whole, they increase the range of feedstocks available for the manufacture of sustainable biodiesel (Neupane, 2022).

The Transesterification Reaction

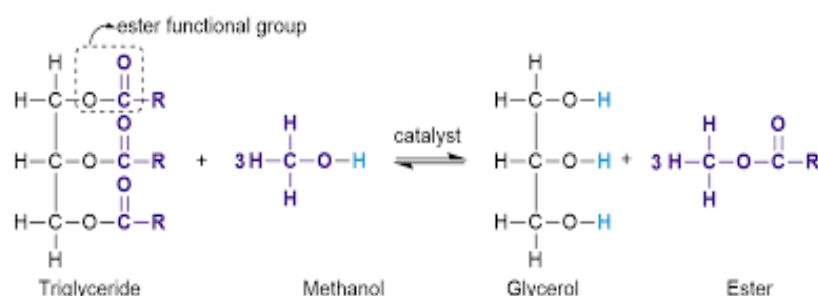


Figure 1: Overall transesterification reaction

Transesterification reaction proceed via three consecutive, reversible steps, which each steps releasing one molecule of fatty acid methyl ester (FAME).

Triglyceride + CH₃OH $\rightleftharpoons$ Diglyceride + FAME
Diglyceride + CH₃OH $\rightleftharpoons$ Monoglyceride + FAME
Monoglyceride + CH₃OH $\rightleftharpoons$ Glycerol + FAME

The catalyst's function in base-catalyzed transesterification starts even before the triglyceride is involved: basic active sites abstract a proton from methanol to produce a nucleophilic methoxide ion. The electrophilic carbonyl carbon of the triglyceride (or, in later stages, the di- or monoglyceride) is then attacked nucleophilically by this methoxide ion, creating a tetrahedral intermediate. The FAME product is released when this unstable intermediate collapses, releasing a diglyceride (or, in subsequent steps, a monoglyceride or glycerol) anion. After that, the diglyceride anion abstracts a proton, completing the catalytic cycle and producing a neutral diglyceride that is prepared for the subsequent methoxide assault, until all three ester bonds are broken and glycerol is completely released, this process is repeated (Zhang *et al.*, 2022).

The planned pathway may be in competition with two side responses. Basic catalysts perform poorly on high FFA feedstocks because saponification happens when free fatty acids or triglycerides react with the basic catalyst (or with hydroxide formed in the presence of trace water) to form soap rather than ester, consuming catalyst and making product separation more difficult. In contrast, esterification is the acid-catalyzed reaction of free fatty acids directly with alcohol to form esters and water. Because it is unaffected by the FFA driven soap formation that causes problems for basic catalysts, this reaction is frequently used as a pretreatment step for high FFA feedstocks prior to base-catalyzed transesterification (Lawal *et al.*, 2018).

Catalysts type, alcohol-to-oil molar ratio, reaction temperature and time, catalysts loading, and feedstock quality (especially FFA and water content) are some of the interacting variables that affect overall transesterification efficiency and must be jointly optimized to maximize biodiesel yield (Zheng & Cho, 2025).

Homogeneous vs Heterogeneous Catalysts

Table 1: Comparison of Catalysts Systems for Biodiesel Production

Property	Homogeneous Catalysts	Heterogeneous Catalysts	Enzymatic Catalysts
Catalytic activity	High	Moderate to high	Moderate
Separation	Difficult	Easy	Moderate (immobilized)
Reusability	Poor	Good to excellent	Good (immobilized)
Wastewater generation	High	Low	Very low
Soap formation	Significant	Minimal	None
Catalyst recovery	Difficult	Easy	Moderate
Relative cost	Low	Moderate to high	High
Tolerance to FFA/water	Poor	Variable (support-dependent)	Good
Industrial adoption	Widespread	Limited, growing	Very limited

Although heterogeneous catalysts have distinct advantages in terms of separation and reusability, their relative cost can be higher than that of simple homogeneous alkalis because of synthesis, activation, or support materials. Additionally, their industrial adoption is still limited when compared to traditional NaOH/KOH-based processes, though this is beginning to change as more affordable, waste-derived alternatives are developed (see Section 4.5).

The alkaline reaction environment encourages corrosion of reactor and pipeline materials; the purification of the biodiesel product necessitates energy-intensive water washing and drying steps; residual catalysts is difficult to completely remove from the biodiesel product, which can affect compliance with fuel quality standards (e.g., ash content, free glycerol); and disposal of the resulting saline wastewater carries its own environmental burden. These practical challenges extend beyond soap formation and wastewater generation (Ruhul *et al.*, 2015)

Important of Basic Active Sites in Transesterification Reaction

An area on a solid catalytic surface that can donate an electron pair or take up a proton from an adsorbing molecule is known as a basic active site. Solid catalysts are affected by two different kinds of basicity. Brønsted basic sites are proton acceptors that can steal a proton from an adsorbed species (like methanol). They are usually surface hydroxyl groups or oxygen anions. Lewis basic sites, on the other hand, are electron-pair donors that supply electron density to a nearby electrophilic center without transferring protons. These sites are typically coordinatively unsaturated oxygen ions (O^{2-}) exposed at surface flaws, edges, or corners. Both site types are present in the majority of solid base catalysts used in the manufacture of biodiesel, including alkaline earth metal oxides like CaO and MgO. The relative amounts of both site types vary depending on the material's crystal structure, surface defect density, and preparation technique (Bing & Wei, 2019)

Heterogeneous catalysts with simple active sites have shown remarkable performance in the production of biodiesel. Methanol molecules are primarily adsorbed and activated by these sites: a basic site removes a proton from methanol to produce a nucleophilic methoxide ion (CH_3O^-), which is the main reactive species in transesterification (Zhang *et al.*, 2024). After attacking the triglyceride's carbonyl carbon, the methoxide ion eventually produces glycerol and fatty acid methyl esters. Catalytic activity is therefore significantly impacted by:

- i. Basic site density
- ii. Basic site strength and type (Brønsted vs. Lewis)
- iii. Accessibility of active sites
- iv. Surface area and porosity

Because materials with plentiful, strong, and accessible basic sites often exhibit superior transesterification activity and higher biodiesel yields, an understanding of the nature and behavior of basic active sites is therefore essential for the rational design of effective heterogeneous catalysts.

Fundamentals of Basic Active Sites

Basic active sites, such as Lewis or Brønsted, were introduced in Section 2.6. This section examines their classification, quantitative measurement, and the structural factors governing their accessibility in greater depth.

Classification Basic Active Sites

Basic active sites can be classified along several independent dimension

By Strength

Based on CO_2 temperature-programmed desorption (CO_2 -TPD) peak temperature, which is a standard analog for basicity strength and a proxy for how firmly a site binds an adsorbed CO_2 probe molecule, sites are typically classified as weak, medium, or strong:

- i. Weak sites: CO_2 desorption below $200^\circ C$; correspond to surface hydroxyl groups
- ii. Medium sites: desorption in the 200 – $400^\circ C$ range; typically metal-oxygen ion pairs
- iii. Strong sites: desorption above $400^\circ C$; associated with low-coordination surface O^{2-} ions

On the Hammett H^- scale, weak base sites are generally defined as $H^- < 9.8$, medium sites as $9.8 < H^- < 15.0$, and strong sites as $H^- > 15.0$, though exact thresholds vary between studies (Bing & Wei, 2019; Zhao *et al.*, 2023). Basic site density is typically reported in μmol CO_2 desorbed per gram or per square meter of catalyst ($\mu mol/m^2$), allowing comparison of site concentration independent of strength.

By Nature

Sites are also classified as Brønsted (proton-accepting, e.g., surface OH^-) or Lewis (electron pair-donating, e.g., coordinatively unsaturated O^{2-}), as introduced in Section 2.6.

By Location

Sites may reside at the outer surface, where they are immediately accessible to reactants, or within the bulk structure, where they contribute little to catalysis unless exposed by defects, doping, or particle fracturing.

By Coordination Environment

The local coordination of surface oxygen atoms affects basicity at the atomic scale: ions at flat terraces are usually less basic than those at step or kink sites, where a lower coordination number increases electron density and reactivity. This distinction becomes particularly important when comparing nanostructured versus bulk catalysts (Section 4.10).

Theoretical Basis: Hard–Soft Acid–Base (HSAB) Theory

For comprehending basic-site reactivity in transesterification, HSAB theory offers a helpful framework. The oxygen in methanol, a comparatively hard base, interacts preferentially with hard Lewis acidic surface cations, and the resulting methoxide ion, a stronger, harder base, combines effectively with the triglyceride's hard, electrophilic carbonyl carbon. Catalysts dominated by hard oxide-ion basicity (e.g., CaO, MgO) are typically successful for this reaction, while softer basic sites typically exhibit lower activity for the comparable nucleophilic attack step (Melnikov *et al.*, 2020)

Origin of Basicity in Solid Catalysts

A solid oxide's basicity results from the electron density localized on its surface oxygen atoms, which is affected by the coordination environment, the electropositivity of the associated metal cation, and the existence of structural defects or dopants that produce more under-coordinated sites (Zuo *et al.*, 2023)

Factors Affecting Basic Active Sites Accessibility

If reactant molecules cannot physically access the strong, plentiful basic sites in a catalysts, the catalyst will operate poorly. This accessibility is determined by several structural factors:

Surface Area

Larger surface areas expose more basic sites per unit mass, increasing the frequency of catalysts reactant contact.

Pore Architecture

IUPAC divides pores into three categories: macroporous (>50 nm), mesoporous (2–50 nm), and microporous (<2 nm). Because triglyceride molecules are far larger than methanol, this distinction is important. Although microporous materials have a huge surface area, they frequently limit triglyceride diffusion to locations inside the pore network, leaving a major portion of that surface area catalytically underutilised. For transesterification, mesoporous and hierarchically porous materials which combine macropores with mesopores are typically chosen because they preserve a large surface area while enabling bulky triglyceride molecules to reach internal active areas

Diffusion Limitations

When reactant transport into the pore network is slower than the intrinsic reaction rate at the active site, the reaction becomes diffusion-limited rather than kinetically limited meaning measured activity reflects transport resistance rather

than true site reactivity. This is described quantitatively by the effectiveness factor (the ratio of observed to intrinsic reaction rate) and the tortuosity factor (which accounts for the non-straight diffusion path through a porous network); low effectiveness factors signal that pore structure, not basicity, is the limiting factor and that catalysts redesign toward larger pores or smaller particles is needed.

Particle Size

Smaller particles reduce the diffusion path length and increase external surface area, both of which lessen diffusion limitations.

Dispersion of Active Species

Uniform dispersion of the active phase (particularly relevant for supported catalysts) prevents agglomeration and maximizes the fraction of basic sites available for reaction. Together, these factors explain why supported and nanostructured catalysts frequently outperform bulk materials of nominally similar basicity their advantage often lies in accessibility rather than intrinsic site strength (Vogt and Weckhuysen, 2022).

Table 2: Classification of Basic Activities

Basic Site Type	Typical Surface Species	CO ₂ -TPD Desorption Temperature	Approx.H. (Hammett) Range	Role in Transesterification
Weak	Surface hydroxyl group (OH ⁻)	<200°C.	H ₊ < 9.8.0	Limited Methanol Activation
Medium	Metal oxygen ion pairs	200–400 °C	9.8 < H ₊ 15.0	Effective, selective methoxide formation
Strong	Low coordination Surface O ²⁻ ions	>400 °C	H ₊ > 15.0	Rapid methanol activation: risk of side reactions if excessive

Classification of Heterogeneous Basic Catalysts

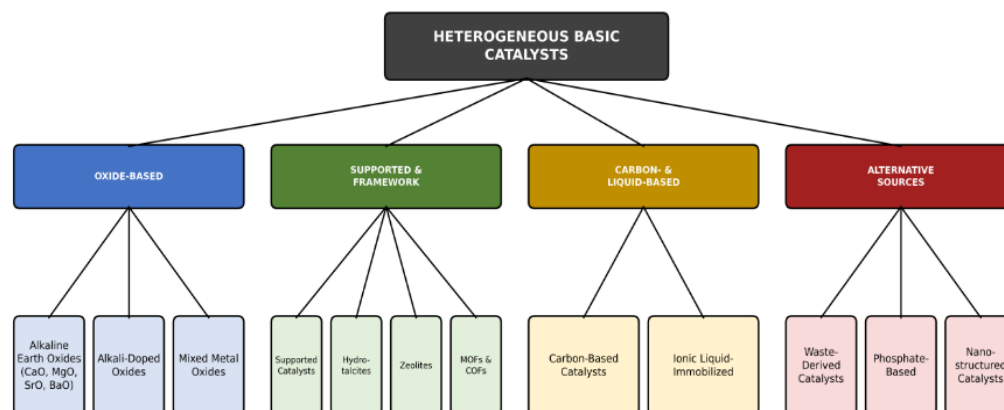


Figure 2: Classification of Heterogeneous basic catalysts by structural category

Alkaline Earth Metal Oxides

Calcium Oxides (CaO)

Because of its strong basicity, natural abundance, low toxicity, and affordability, calcium oxide is the most researched heterogeneous basic catalysts for the production of biodiesel. CaO has a rock-salt (cubic) crystal structure, and low-coordination surface O²⁻ ions exposed at edges, corners, and defect sites are the main source of its catalytic activity. Since these under-coordinated ions are significantly more basic than O²⁻ in the well-ordered bulk lattice, surface defect density, which is influenced by particle size and preparation technique, directly controls activity. CaO based catalysts have been shown to provide biodiesel yields of over 90% under ideal circumstances. Additionally, CaO can be easily obtained from waste items high in calcium, such as limestone,

eggshells, and snail shells (Section 4.4). CaO's basicity and activity are significantly impacted by calcination temperature: calcination must be sufficient to completely break down the calcium carbonate/hydroxide precursor to CaO (usually requiring temperatures above ~800°C; excessive calcination can result in sintering and surface area loss, while incomplete calcination leaves residual carbonate that blocks basic sites (Mazaheri *et al.*, 2021).

CaO has three main deactivation mechanisms despite its high activity. When surface CaO and ambient or feedstock moisture combine to generate Ca(OH)₂, which is less basic than CaO itself, hydration takes place. Unprotected CaO catalysts deteriorate not only during use but also during storage due to carbonation, which happens when ambient CO₂ interacts with surface sites to generate CaCO₃, directly

blocking basic sites. This process is thermodynamically favourable even at room temperature. Calcium species leaching into the reaction medium (especially when methanol, glycerol, or free fatty acids are present) lowers catalysts mass over subsequent cycles and contaminates the biodiesel product with residual calcium, which may have an impact on fuel quality standards (Mazaheri *et al.*, 2021).

The impurity profile is a source of the batch-to-batch variability frequently reported for CaO derived from waste sources because trace impurities (such as Mg, Sr, P, and Na from bone or shell matrices) can either enhance basicity through minor doping effects or, if present as inert phases, dilute active site density (Section 4.4). Doping CaO particles with alkali or alkaline earth metals to increase surface defect density, coating CaO particles with a protective layer (such as a thin silica or polymer shell) to slow moisture CO₂ ingress, and supporting CaO on a secondary oxide to physically separate and stabilise active particles against sintering and leaching are some of the methods to improve CaO stability that have been reported (Fu *et al.*, 2026).

Related to CaO, calcium hydroxide [Ca(OH)₂] has also been directly employed as a heterogeneous basic catalysts for biodiesel production from unconventional lignocellulosic feedstocks under mild conditions (Ali *et al.*, 2026). (see Section 4.3, Supported Catalysts).

Magnesium Oxides (MgO)

Another extensively researched alkaline earth oxide catalyst is magnesium oxide, which is prized for its superior thermal stability and resistance to hydration in comparison to CaO. This resistance results from MgO's stronger Mg-O bonding and higher lattice energy, which make surface hydroxylation and rehydration less thermodynamically favourable than in CaO. However, the same structural stability also means that MgO exposes fewer highly reactive low coordination O₂⁻ sites, which leads to weaker overall basicity and generally lower transesterification activity than CaO when used alone (Julkapli & Bagheri, 2016).

Potassium, sodium, or lithium species deposited on the MgO surface create additional strong basic sites and can significantly increase methanol activation and reaction rate, effectively combining MgO's structural stability with alkali-derived basicity (see also Section 4.1.5). This technique is commonly used to enhance MgO in order to overcome this limitation. For similar reasons, MgO is frequently employed as a support or added to mixed oxide systems (section 4.2).

Strontium Oxides (SrO)

Due to its larger ionic radius and hence higher surface reactivity, strontium oxide is more basic than both CaO and MgO. It has also shown outstanding transesterification efficiency with quick methanol activation. But because of this same reactivity, SrO is very reactive toward air CO₂, generating SrCO₃, and strongly hygroscopic, easily absorbing atmospheric moisture to generate Sr(OH)₂. This means that although while SrO based catalysts have great intrinsic activity, their industrial use has been limited since they must be stored in an inert or moisture-free environment and are prone to quick deactivation upon contact to ambient air (Tavizon-pozos & Cruz-Aburto, 2024).

Barium Oxides (BaO)

Among the common alkaline earth oxides, barium oxide exhibits the strongest basicity and has produced large amounts of biodiesel in lab experiments. However, the toxicity of barium compounds poses a serious threat to human health and the environment, which raises issues about worker

safety when handling catalysts and about Ba²⁺ seeping into wastewater streams or biodiesel. These toxicity issues, together with catalyst stability issues akin to those affecting SrO, have generally prevented BaO from being used in actual industrial applications and instead restricted it to a comparative or research role (Loh *et al.*, 2025).

Alkali Metal-Doped Alkaline Earth Metal Oxides

Doping alkaline earth oxides (especially MgO and CaO) with alkali metals (K, Na, and Li) produces more strong basic sites than the parent oxide alone because the alkali metal introduces new, highly electropositive surface species that donate electron density more readily than the native oxide ions (see Section 4.1.2). Since the resultant materials frequently outperform either the parent oxide or the alkali salt alone, combining the structural robustness of the alkaline earth oxide with alkali-enhanced basicity, this doping method is currently regarded as a separate catalyst design approach in and of itself (Bingwa *et al.*, 2018).

Mixed Metal Oxides

In order to take use of complementing qualities that single oxides cannot, mixed metal oxides combine two or more metal components. There are two possible structural configurations: a composite, where different oxide phases coexist with defined boundaries, or a solid solution, where cations of various metals are uniformly distributed within a single crystal lattice, creating structurally uniform basic sites throughout the material. Catalytic enhancement in composites frequently starts at the interface between phases, where different electronegativities and lattice mismatch produce new coordinatively unsaturated oxygen environments with basicity different from either parent oxide. This interfacial contribution is often the main cause of the "synergistic effect" observed in mixed oxide studies, rather than just additive basicity from both components (Gao *et al.*, 2023).

MgO-Al₂O₃ and MgO-MgAl₂O₄ (spinel-forming systems offering improved thermal stability), CaO-CeO₂ (where CeO₂'s oxygen-storage capacity is reported to help stabilise surface oxide vacancies), and KF/Zn(Al)O (where fluoride doping enhances basicity of the underlying mixed oxide) are examples of representative systems. In all of these systems, the metal ratio is a crucial design variable. While excess of either component tends to simply dilute activity with a less active bulk phase, an ideal ratio usually maximises interfacial or defect-site density. Compared to single oxides, mixed metal oxides often exhibit better basic site density, active-site accessibility, and resistance to deactivation; biodiesel yields above 90% have been shown in a number of these systems (Fan *et al.*, 2025).

Supported Catalysts

Supported catalysts improve the dispersion and accessibility of active sites while lowering the mass of costly or rare active material needed by dispersing an active basic phase (such as an alkali metal salt or alkaline earth oxides) onto a high-surface-area, structurally sound support (such as alumina, silica, or zeolite). For instance, KOH impregnated on alumina has shown substantial transesterification activity by combining the high intrinsic basicity of KOH with the textural characteristics of alumina (Feng *et al.*, 2015). Similar to this, MgO/ZnO supported on γ -Al₂O₃ has demonstrated good reusable performance in a variety of oil and alcohol combinations, which is explained by the amphoteric nature of ZnO and the fundamental characteristics of Mg species.

Waste-Derived Catalysts

Waste-derived catalysts, which are made from calcium-rich biological waste including eggshells, snail shells, and bone material, provide an affordable and sustainable way to produce active CaO-based catalysts by adding value to waste streams that would otherwise need to be disposed of. In comparison to undoped waste-derived CaO, doping these materials with alkali metals (e.g., K, Sr) has been demonstrated to significantly improve both initial yield and reusability (Tavizón-Pozos *et al.*, 2025). Their performance and stability are heavily dependent on the trace impurity profile inherited from the source material (Section 4.1.1).

Hydrotalcites

Rehydrated hydrotalcites have shown excellent performance as heterogeneous methanolysis catalysts for biodiesel synthesis, and hydrotalcites (Mg-Al layered double hydroxides) offer variable basicity through adjustment of the Mg:Al ratio and calcination conditions (Yan *et al.*, 2017).

Phosphate Based Catalysts

One less popular but efficient class of solid base catalysts is metal phosphates. For instance, when calcined at regulated temperatures, sodium phosphate (Na_3PO_4) has shown good transesterification activity with stable, reusable performance, and its basicity may be adjusted by calcination temperature (Jawad *et al.*, 2023). Compared to simple oxide catalysts, phosphate-based catalysts are typically appreciated for their resistance to leaching and thermal stability.

Zeolites and Molecular Sieves

Zeolites are crystalline aluminosilicates whose basicity can be adjusted by exchanging alkali-metal ions (such as Na, K, and Cs). The electropositivity of the swapped cation increases the basic strength. However, because of their microporous structure, conventional three-dimensional zeolites frequently have low base site density and severe mass-transfer limitations. To address this, two-dimensional and hierarchically porous zeolites have been developed, which provide greater external surface area and improved site accessibility for bulky triglyceride molecules (Wang *et al.*, 2026).

Metal Organic Framework (MOFs) and Covalent Organic Framework (COFs)

MOFs are crystalline porous materials with remarkably large and adjustable surface areas that are constructed from metal nodes joined by organic linkers. Strong transesterification performance has been demonstrated by basic and bifunctional MOF-based catalysts, and MOF-derived mixed oxides (such as calcining a Zn/Mg MOF precursor to produce a stabilised MgO/ZnO composite) provide a pathway to well-dispersed, high-surface-area basic catalysts (Cong *et al.*, 2021). Although their use in base-catalyzed (as opposed to acid-catalyzed) transesterification is still relatively underdeveloped, COFs, an analogous class constructed from covalent rather than coordination bonds, offer comparable structural tunability with generally superior chemical stability.

Carbon Based Catalysts

Solid base catalysts can be produced by functionalising activated carbon and compounds obtained from biochar, usually through nitrogen doping. For instance, nitrogen-doped hierarchical porous carbons offer high surface area, a large number of easily accessible basic sites, and good hydrophobicity and wettability for oil-phase reactants

qualities that are ideal for transesterification (Shetty *et al.*, 2022).

Nanostructured Catalysts

According to comparison to bulk materials of the same composition, nanostructured basic catalysts, such as nanoscale CaO and MgO, achieve enhanced basicity and activity by taking advantage of high surface-area-to-volume ratios and an increased proportion of low-coordination surface sites (edges, corners, kinks; Section 3.2). For example, under ideal circumstances, Nano-CaO has shown biodiesel yields of 96% (Bano *et al.*, 2020).

Ionic Liquid Immobilised Catalysts

The separation and viscosity constraints of liquid-phase ionic liquid catalysts can be addressed by immobilising basic ionic liquids on porous supports, such as MOFs, to combine the ionic liquid's adjustable basicity with a solid support's recoverability. It has been demonstrated that this immobilisation technique significantly lowers active-phase leaching in comparison to straightforward impregnation while maintaining high catalytic activity over several cycles (Pedro *et al.*, 2019).

Catalysts Deactivation and Regeneration

Basic heterogeneous catalysts have considerable intrinsic activity, but their industrial viability is limited by a number of deactivation mechanisms: Surface basic sites, especially O^{2-} ions, combine with air or dissolved CO_2 to generate surface carbonates, which are catalytically inactive. This process is known as carbonation. For CaO and SrO, this is frequently the predominant deactivation pathway, not just during reaction but also during storage (Argyle & Bartholomew, 2015).

Hydration is the result of moisture reacting with the catalyst surface to produce hydroxides, which are less basic than the parent oxide. Similar to carbonation, this can happen both during storage and during a reaction. It is especially problematic for hygroscopic materials like SrO (Dias & Ramos, 2021).

Leaching is the process by which active metal species (such as Ca^{2+} and Sr^{2+}) dissolve in the reaction medium due to the polar reaction environment (methanol, glycerol, and trace water). Leaching contaminates the biodiesel product and decreases catalyst mass during subsequent cycles. When free fatty acids (FFAs) in lower-quality feedstocks react with basic sites to form soap, they consume active catalysts and complicate downstream separation. This process is known as saponification, or poisoning by free fatty acids. Surface area and basic site density are decreased by sintering the coalescence of small particles or crystallites at high temperatures. This is especially important during high-temperature calcination or regeneration steps (Sadaba *et al.*, 2015).

Although it is more frequently linked to acid-catalyzed reactions, coke deposition can also happen when organic residues build up on the catalyst surface and physically obstruct active sites. Because of compositional diversity, the relative importance of these mechanisms varies by catalyst class: carbonation/hydration limits CaO and SrO, leaching limits supported catalysts, and all of the above limits waste-derived catalysts (Lakhani & Srifa, 2026).

Regeneration techniques differ accordingly: high temperature calcination can reverse carbonation and hydration by breaking down surface carbonates and hydroxides back into the active oxide, but repeated calcination cycles run the danger of cumulative sintering and

surface area loss. Soap and organic residue can be eliminated by following washing procedures. However, leaching resistance is prioritised at the catalyst design stage (e.g., through supporting or doping strategies discussed in Sections

4.2 and 4.3) rather than after the fact because regeneration is typically ineffective for leached catalysts because the active phase itself has been lost (Katajisto, 2020)

Consolidate Performance Data

Table 3: Performance of Heterogeneous Basic Catalysts in Biodiesel Production

Catalyst	Biodiesel Yield	Key Condition	Reusability	Source
Nano-CaO	96.2%	65 °C	5 cycles	Harsha Hebbar <i>et al.</i> ,2018
MgO (Carbon-Supported)	96.5%	75 °C	5 cycles (85.7% retained)	Du <i>et al.</i> ,2019
SrO	98.2%	80 °C	5 cycles (>90.7% retained)	Roschat <i>et al.</i> ,2018
Ca--rich mixed oxide	96%	65 °C	4 Cycles, Stable	Cakirca & Akin,2025
CaO (K-Sr doped ,eggshell)	92.5%	70 °C	3 cycles (~72% retained)	Tavizon-pozos <i>et al.</i> ,2025
Mg-Al hydrotalcite	High	Moderate tempreture	Good Stability	Navajas <i>et al.</i> ,2018
K2O/Zn-aluminate (supported alkali)	96. %	70 °C	4 cycles	Mirshafiee & Rezaei 2025
MgO/Carbonate (Na ₂ CO ₃ or K ₂ CO ₃)	95.8—97.5%	600 °C Calcination	Not reported	Li <i>et al.</i> ,2025

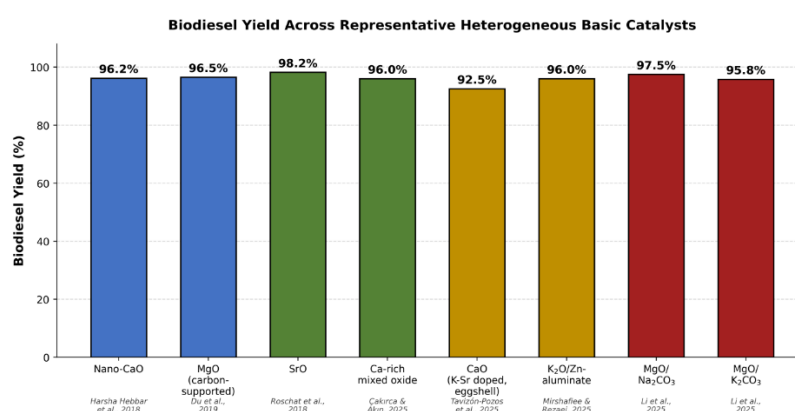


Figure 3: Biodiesel yield comparison across representative heterogeneous basic catalysts, compiled from the studies in Table 3

Characterization and Evaluation

Since no single method fully captures the key features of a catalysts, it is necessary to combine numerous characterisation techniques in order to arrive at reliable structure-performance conclusions. The following methods are categorised according to the information they provide: bulk composition, surface chemistry and basicity, textural qualities, and structural/phase composition.

Textural Characterisation

BET analysis uses cryogenic temperature measurements of nitrogen (or argon) adsorption-desorption isotherms to calculate surface area, pore volume, and pore size distribution. BET measurements are crucial for evaluating accessibility for basic catalysts (Section 3.5). If triglycerides are unable to diffuse to interior locations, a catalyst with high basicity but a BET-measured microporous shape may nevertheless operate poorly. To determine whether measured surface area corresponds to true porosity or just small particle size, BET is usually combined with TEM or SEM (Villarreal-Rocha *et al.*,2021). One major drawback of BET is that it relies on a particular isotherm model (either BET or BJH); findings may be deceptive for materials with considerable microporosity or irregular pore geometries, in which case supplementary techniques (such DFT-based pore analysis) are recommended.

SEM is frequently used in conjunction with EDS (energy-dispersive X-ray spectroscopy) for elemental mapping, which is helpful for verifying dopant distribution in mixed oxides or identifying impurity elements in waste-derived catalysts.

SEM offers surface morphology and particle size/shape information at micron-to-submicron resolution. At the expense of more difficult sample preparation and a much smaller sampled area (raising representativeness concerns unless multiple fields are imaged), TEM extends this to the nanoscale, resolving individual nanoparticle size, crystallite morphology, and lattice fringes for crystalline phase identification (Burmana & Manurung,2026).

Structural and Phase Characterization

Essentially comparing diffraction peak positions and intensities to reference patterns, XRD can identify crystalline phases in a catalyst. For instance, it can confirm that calcination has completely converted a CaCO₃ precursor to CaO or identify residual carbonate/hydroxide phases that indicate incomplete activation or post-synthesis carbonation (Bulavchenko & Vinokurov, 2023). The Scherrer equation can also be used to determine crystallite size using peak broadening. A catalysts can exhibit a "clean" XRD pattern while still containing catalytically significant minor or amorphous species due to XRD's primary sensitivity limitation: amorphous phases and species present below about 5% by mass are usually invisible. For this reason, XRD is typically combined with CO₂-TPD (see below) to correlate bulk phase composition with actual basicity (Khan *et al.*, 2020).

Into addition to tracking structural evolution during synthesis, calcination, and reaction, FTIR can identify surface functional groups (such as hydroxyl, carbonate, and metal-oxygen vibrations) (Jambhulkar *et al.*, 2022). For example, it

can identify the appearance of carbonate bands as a fingerprint of catalyst carbonation during storage or use.

Determining appropriate calcination and regeneration temperatures is directly related to TGA (thermogravimetric analysis), which measures mass loss as a function of temperature and reveals moisture content, thermal stability limitations, and the breakdown of precursor phases (carbonates, hydroxides) (Section 4.12).5.3 Characterisation of Surface Chemistry and Basicity

Surface Chemistry and Basicity Characterization

The main method for measuring basic site strength and density is CO₂-TPD; typical temperature ranges reported in Table 2). In a typical experiment, CO₂ is adsorbed onto the catalyst surface at low temperature and then desorbed under a controlled temperature ramp while desorption is monitored (usually by mass spectrometry or TCD); the integrated peak area (calibrated against a known CO₂ volume) provides site density in μmol/g, and the desorption temperature of each peak indicates site strength (Papargyriou *et al.*, 2019). The likelihood of surface carbonate production being misinterpreted and the potential for CO₂ re-adsorption on nearby sites during heating, which might artificially move or broaden peaks, are important limits. Complementary probe molecules, including pyrrole or SO₂, are occasionally used in conjunction with CO₂ to cross-validate site character for true basic-site desorption (Etim, 2022).

Rather than being only a less sophisticated substitute for CO₂-TPD, Hammett indicators are the sole technique that offers an absolute basicity scale (the H₋ value), which is based on the colour shift of adsorption indicator dyes with known pK_a values (Zhao *et al.*, 2023). Their main drawbacks are that they cannot be used with opaque or coloured catalysts (colour changes cannot be seen) and they depend on the establishment of real adsorption equilibrium, which is not always easy to verify. When used in conjunction with CO₂-TPD, Hammett titration offers an absolute strength benchmark that enhances the more accurate but relative strength-distribution data from CO₂-TPD.

X-ray photoelectron spectroscopy, or XPS, is useful for determining the oxidation state of active metal species and differentiating surface enrichment or depletion of particular elements (relevant to doped or mixed oxide catalysts). It does this by probing the surface elemental composition and oxidation states within the top few nanometres. Temperature-programmed reduction, or TPR, gauges a catalyst's reducibility and provides information on the oxidation state

and strength of the metal-oxide interaction. This is especially important for mixed and supported oxide systems, where redox behaviour can affect basicity (Sambalova *et al.*, 2020).

Bulk Composition and Structure

Bulk elemental composition is provided by XRF (X-ray fluorescence), which is helpful for verifying dopant loading or measuring impurity level in catalysts generated from waste. Nuclear magnetic resonance (NMR), especially solid-state ²⁷Al or ²⁵Mg NMR, can investigate local coordination environments in catalysts containing aluminate or magnesium, providing structural detail in addition to the long-range crystallinity data provided by XRD (Loy *et al.*, 2024)

Integrated Characterization

Catalytic performance cannot be fully explained by a single method; complementing approaches must be used to draw reliable structure-activity findings. BET with TEM/SEM (correlating surface area with real pore/particle architecture), CO₂-TPD with XRD (correlating basicity with bulk phase composition), and XPS with CO₂-TPD (connecting surface elemental/oxidation-state chemistry to observed basic-site density) are examples of common pairings. A typical flaw in the literature on biodiesel catalysis is reliance on a single approach, which puts performance variations at danger of being mistakenly attributed to the wrong underlying cause (Abo & Areti, 2025).

Reaction Performance Evaluation

Beyond catalysts characterisation, reporting biodiesel yield alone is insufficient for meaningful performance evaluation. Intrinsic catalytic activity can be compared regardless of reaction time or scale thanks to reaction kinetics (rate constants, activation energy, and turnover frequency). Because side reactions (Section 2.4) might result in significant triglyceride conversion without correspondingly high biodiesel-quality product, selectivity of the FAME profile and glycerol purity obtained matters. Kinetic experiments at different stirring speeds should be used to verify mass transfer constraints (Section 3.5); if the rate is stirring-independent, the reaction is kinetically controlled, whereas stirring-dependence indicates an external mass transfer limitation. Lastly, the conventional technique for differentiating true heterogeneous catalysis from homogeneous catalysis is hot filtration assays, which remove the solid catalysts halfway through the reaction and verify the reaction does not continue in the filtrate (Mansir *et al.*, 2017).

Table 4: Characterization Techniques for Heterogeneous Basic Catalysts

Category	Techniques	What it Reveals
Textural	BET, SEM/EDS, TEM	Surface area, pore structure, morphology, particle size
Structure/Phase	XRD, FTIR, TGA	Crystalline phases, Functional groups, thermal stability
Surface Basicity	CO ₂ -TPD, Hammett indicators	Basic sites strength & density (relative and absolute scales)
Surface Chemistry	XPS, TPR	Oxidation states, surface composition, reducibility
Bulk Composition	XRF, NMR	Elemental Composition, Local coordination

Challenges and Future Perspectives

Deactivation mechanisms: Summary and Mitigation

Section 4.12 detailed the chemistry of carbonation, hydration, leaching, poisoning, sintering, and coke deposition. Their

relative severity and appropriate mitigation strategy differ by catalyst class:

Table 5: Deactivation Mechanisms and Mitigation Strategy

Mechanism	Most Affected Catalysts	Primary Mitigation
Carbonation /hydration	CaO, SrO, BaO	Inert syroge; protective coatings; alkali doping
Leaching	Supported and mixed oxides catalysts	Stronger metal-support binding encapsulation
FfA poisoning (soap formation)	All basic catalysts,esp.with low quality feedstock	Feedstock pretreatment
Sintering	All classes,during calcination/ regeneration	Controlled calcination temperture; structural promoters
Coke deposition	Less common: carbon-based/supported catalysts	Periodic oxidative regeneration

Emerging Technology and Specific Research Directions

Rather than simply making generalisations about "improved stability," a number of specific, cutting-edge strategies are worth considering. The search for ideal compositions beyond trial-and-error synthesis is accelerated by machine learning-assisted catalyst discovery, which correlates catalyst physicochemical descriptors with performance (Bozal-Ginesta *et al.*, 2025). However, experimental validation of improvements in heterogeneous catalysis is still limited in comparison to computational predictions. Compared to the single-variable optimisation prevalent in the current literature on biodiesel catalysis, combining such models with high-throughput experimentation ystematic, automated synthesis and testing of catalyst libraries offers a way to more effectively explore doping ratios, support combinations, and synthesis conditions.

By enhancing mixing and heat/mass transfer through high surface-area-to-volume geometries, continuous-flow reactor systems (packed-bed, microreactor, and oscillatory flow configurations) address a major drawback of batch heterogeneous catalysis: mass transfer between the oil, alcohol, and solid catalyst phases. These systems are increasingly seen as essential for converting lab-scale heterogeneous catalyst performance to industrial throughput (Gopi *et al.*, 2022).

Because they have both acid and base sites, bifunctional catalysts enable the simultaneous esterification (of free fatty acids) and transesterification (of triglycerides) in a single step, providing a direct method of processing high-FFA feedstocks of lower quality without the need for an additional pretreatment step (Welter *et al.*, 2023). This idea also applies to tandem catalytic systems, which simplify multi-step conversions by combining sequential or spatially separated catalytic functions within a single reactor.

Industrial Implementation Barriers

Beyond general cost issues, industrial adoption of heterogeneous basic catalysts is subject to particular requirements: catalysts must perform consistently across feedstock batches of varying quality, maintain mechanical strength and attrition resistance under continuous reactor operation (especially in fixed-bed or fluidised configurations), and sustain activity over a lifetime long enough to offset synthesis cost. Laboratory-optimized catalysts are rarely tested against these requirements (Jimenez *et al.*, 2026). Because trace catalysts leaching into the product must stay within predetermined ash and metal content limitations, regulatory certification for biodiesel fuel quality requirements (such as ASTM D6751, EN 14214) indirectly restricts catalyst choice.

Sustainability Assessment

A comprehensive sustainability picture necessitates taking into account of the energy intensity of catalysts synthesis (e.g., calcination temperatures frequently exceeding 600–800°C are energy-intensive at scale), the source of raw materials (waste-derived catalysts, Section 4.4, offer a

genuine sustainability advantage by valorising agricultural or industrial waste streams rather than consuming virgin mined material), and the end-of-life fate of spent catalysts. There is a glaring research vacuum and a dearth of formal life-cycle assessment comparing catalysts classes on these parameters in the literature.

Biocatalytic Alternatives

Although solid base catalysts have been the main focus of this analysis, enzymatic (lipase-based) catalysis is an important supplementary strategy. While whole-cell biocatalysts (such as yeast expressing lipase or engineered *E. coli*) and immobilised lipases can catalyse transesterification under mild conditions with high selectivity and tolerance to FFA-containing feedstocks, their slower reaction rates and higher cost have limited their industrial adoption in comparison to chemical catalysts (Zhao *et al.*, 2024). An understudied approach to processing mixed-quality feedstocks is hybrid systems that combine a solid base catalyst with an immobilised enzyme, utilising the base catalyst's speed and the enzyme's FFA tolerance.

Feedstocks Flexibility

The vulnerability of basic catalysts to saponification continues to limit the processing of high-FFA, high-water feedstocks (Section 2.2, waste oils, and low-grade fats). This is addressed by two proven methods: a two-step procedure that uses acid-catalyzed esterification to lower the FFA level prior to base-catalyzed transesterification, and feedstock preparation (such as degumming or drying) to eliminate water and phospholipids prior to reaction (Hamood ur Rehman *et al.*, 2025). A way to combine both processes in a single reactor and maybe lower the additional cost of feedstock flexibility is using bifunctional catalysts (Section 6.2).

Integration with Downstream Processing

More than only reaction yield is impacted by catalysts selection; residual catalysts or leached metal species may influence biodiesel's adherence to ash and metal-content fuel requirements, necessitating further purification. The main byproduct, glycerol, is a valuable co-product that can be valued into higher-value chemicals, but catalysts leaching and soap formation during reaction directly affect its purity. As a result, catalysts and downstream process design should be considered jointly rather than separately, an integration that is rarely explicitly discussed in the literature currently available on biodiesel catalysis (Sadeghpour *et al.*, 2025).

CONCLUSION

For the synthesis of biodiesel, heterogeneous catalysts with basic active sites have become attractive substitutes for homogeneous alkaline catalysts because they provide simpler separation, reusability, and less wastewater creation. The density, strength, and accessibility of basic active sites factors that affect how well a catalysts activates methanol to create the reactive methoxide species essential to transesterification are the main determinants of catalytic performance.

This review examined the full spectrum of basic heterogeneous catalysts from well-known alkaline earth oxides (CaO, MgO, SrO, BaO) and their alkali-doped and mixed-oxide derivatives, through waste-derived, hydrotalcite, and nanostructured materials, to less well-known classes such as phosphates, zeolites, MOFs, COFs, carbon-based, and ionic liquid-immobilized catalysts.

In comparison to single oxides, mixed oxide and supported systems typically increase stability and active-sites accessibility, frequently through interfacial or defect-sites contributions as opposed to straightforward additive basicity. Since no single method fully captures the picture, reliable structure-performance conclusions rely on combining several characterisation techniques: textural (BET, SEM, TEM), structural (XRD, FTIR, TGA), and surface-chemical (CO₂-TPD, Hammett titration, XPS). Additionally, performance is evaluated using kinetics, selectivity, and hot-filtration leaching tests rather than yield alone.

Catalysts deactivation (carbonation, hydration, leaching, and FFA poisoning), feedstock quality limitations, and the disconnect between laboratory-optimized and commercially feasible synthesis methods continue to be the key obstacles to widespread use despite significant advancements. Bifunctional catalysts that can directly process lower-quality feedstocks, continuous-flow reactor systems appropriate for industrial throughput, computational and machine learning-assisted catalysts design, and a more rigorous, standardised approach to reporting reaction conditions and reusability data across the field an inconsistency that currently makes cross-study comparison challenging will probably be necessary to address these. Transforming the robust laboratory performance of basic heterogeneous catalysts into a really industrially viable pathway to sustainable biodiesel production would require overcoming these obstacles.

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