

Deactivation Processes, Regeneration Conditions and Reusability Performance of CaO or MgO Based Catalysts Used for Biodiesel Production—A Review

Nombamba Oueda¹, Yvonne L. Bonzi-Coulibaly¹, Igor W. K. Ouédraogo^{2*}

¹Laboratory of Analytical, Environmental and Bio-Organic Chemistry, Chemistry Department, UFR-SEA, Université Ouaga I Pr Joseph KI-ZERBO, Ouagadougou, Burkina Faso

²Biomass Energy and Biofuels Laboratory (LBEB), International Institute for Water and Environmental Engineering (2iE), Ouagadougou, Burkina Faso

Email: oudanombamba@yahoo.fr, yvonne.bonzi@yahoo.fr, *ouedigor@yahoo.fr

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Abstract

The activity of a catalyst in transesterification reaction usually declines with repeated uses and this limits the possibility to use it many times. This paper presents a review of various techniques used to evaluate the activity changes, the recycling processes for calcium and magnesium oxides based heterogeneous catalysts for biodiesel production. The activity of calcium and magnesium oxides based catalysts declines due to leaching, surface or active sites poisoning by reactant or product molecules and modification of physical aspects. Physico-chemical methods (AAS, BET, CO₂-TPD, EDS, FTIR, ICP-AES, SEM, TG/DTA and XRD) were used to check the catalyst modification and to confirm the deactivation. When separated from the reaction mixture by filtration, the catalyst could be reused without any treatment or recycled by washing, drying or/and recalcination. Between various recycling processes for calcium and magnesium oxides based catalysts, mixed oxides showed less leaching and performed FAME or FAEE yield >90% with reusability.

Keywords

Deactivation, Recycling, Metal Oxides Catalyst, Transesterification, Biodiesel

1. Introduction

Various processes have been used for biodiesel production through transesterification reaction of triglycerides from vegetable oils, animal fats, and algal oils with methanol (MeOH) or ethanol (EtOH). The key issue of biodiesel quantita-

tive and qualitative production process in developing countries is the applicability and profitability with an environment-friendly process [1] [2] [3]. The economic feasibility of biodiesel production and its intensive commercialization were strongly linked to the feedstock, the alcohol and the catalyst property, availability and cost. In this approach, major research efforts focused on the choosing and testing of catalyst for the transesterification reaction. Heterogeneous catalysts, acidic, basic or neutral provide many advantages in the process such as less corrosive character, simple operating steps, safer handling of material, easy and cheap separation process of biodiesel from the reaction mixture, and little wastewater generation [3]. Between heterogeneous catalysts reported in literature for transesterification in biodiesel production, a large number of metal oxides offer an attractive alternative to overcome economic and environmental drawbacks of homogeneous catalysts [3] [4] [5] [6] [7]. One can note among them, alkaline earth metal oxides (BaO, CaO, MgO) and SrO [8]. Listed in literature and used in transesterification, catalysts based calcium and magnesium oxides provided many advantages for instance; they could be prepared with high purity, possess great activity due to their higher basicity, have long catalyst lifetime, could run under moderate reaction conditions, and are capable of producing high biodiesel yield [4] [5] [9]. When CaO and MgO are doped with other oxides, this enhances their catalytic performance. Therefore, some mixtures were prepared and applied in order to improve the catalyst basicity and stability [10]. Many studies are cited in literature: CaO/MgO [11] [12], CaO/CeO [13], CaO/ZnO [11] [14] [15], CaO/ZrO₂ [16] [17], MgO/SrO [9], CaO/aluminate [18], CaO/silicate [19] [20], Mg/Al oxides [18] [21] [22] [23], CaO/MgFe₂O₄ [24], CaO/activated charcoal [25], CaO-KF [26] [27] [28] [29], MgO/KOH [30], Ti/MgO [31], MgO/chitosan [32], and CaO/zeolite [33].

In addition, both calcium and magnesium are earth metals that could be found in nature [4] [34] [35] [36]. Between potential environmentally friendly resources, dolomite, calcite, hydrotalcite, and hydrocalumite composed essentially of CaCO₃ or with MgCO₃ are used. Bentonite is also natural clay with various proportions of elements: Ca, Na, Al, K, Fe, Mg. Hydrotalcite or magnesium slag, as wastes is calcinated to give Mg-Al and Mg-Ca oxides [4].

Many calcium oxides derived from other natural sources are renewable and abundantly cited in literature. Some are recently prepared from eggshells [4] [37], mud clam shell [38], shells of crab [4] [39], snails shells [40], capiz [41], *Cyrtopleura costata* seashells [42], and mussel shells [43]. After transesterification reaction in biodiesel production, the contaminants of the used catalysts are acyl ester, alcohol, water, free fatty acid, glycerol and soap [44] [45]. In this case, deactivation of the catalyst occurs due to the presence of these various compounds. Many papers described the preparation and performance of solid metal oxide catalysts. Reviews on the Ca and Mg oxides based catalysts mentioned clearly the performance of fresh catalysts. Some results showed the recycling conditions of CaO and MgO based catalysts in biodiesel production. In terms of reusability, the catalysts were not systematically assessed. To help in the research

for an innovative sustainable condition and economical processes for biodiesel production, there is a need to highlight the optimal conditions for reusability of metal oxides in transesterification reaction. In order to increase the knowledge on catalyst reusability, we propose to present the deactivation and activation issues of CaO and MgO based catalysts. The good understanding of the mechanism of a catalyst deactivation will help to plane its regeneration process in biodiesel production. This review will present the mechanisms of activation and deactivation of CaO and MgO based catalysts, the specificity on analytic methods used to describe the physico-chemical changes during successive uses, the recycling conditions and the reusability performance of these catalysts.

2. Mechanistically Approach for CaO/MgO Based Catalyst Activation/Deactivation

2.1. Active Phase of CaO Based Catalyst under Transesterification Reaction

Many different studies reported the active phase of CaO-catalyzed transesterification. This section deals with latest studies that investigated CaO active phase by using analytical approaches. The catalytic effect of CaO in transesterification reaction is due to the oxygen anion presented on the CaO surface. Chemically, CaO is an alkaline earth metal oxide with the ionic crystal structure. The calcium cation is a very weak acid. Therefore, the conjugated oxygen anion displays a strong basic property [44]. The catalytic role of a basic site generated on the surface of CaO particles is to create nucleophilic alcoxides from alcohol, thus initiating the base-catalyzed reaction. Is the case of methanolysis, calcium methoxide $\text{Ca}(\text{OCH}_3)_2$, can be formed on the surface of CaO by action of methanol. This catalyst is known to be highly active in methanolysis of triglycerides. Liu *et al.* [46] studied calcium methoxide as a solid base catalyst to catalyze the transesterification of soybean oil to biodiesel and found that it exhibited excellent catalytic activity, stability and a long catalyst lifetime. Kouzu *et al.*, [47] investigated calcium oxide evolution under transesterifying conditions. They suggested that calcium oxide could be the real active phase at the beginning of the methanolysis of triglycerides, as calcium methoxide did not appear after 15 min of the reaction time. They showed the possible formation of the methoxide anion from the reaction between CaO and methanol. Surface O^{2-} extracts an H^+ and Ca^{2+} adsorbs CH_3O^- from CH_3OH to form CH_3O^- and H^+ on the surface. On the other hand, they found another calcium compound acting as the catalytic active phase after an appreciable amount of glycerol was co-produced (*i.e.* around 30 min of reaction). CaO reacted with glycerol produced under the transesterifying condition to generate calcium diglyceroxide $\text{Ca}(\text{O}(\text{OH})_2\text{C}_3\text{H}_5)_2$. Therefore, the active phase that catalyzes the reaction in this case was estimated as $\text{CH}_3\text{O}-\text{Ca}-\text{O}(\text{OH})_2\text{C}_3\text{H}_5$. Recently, Kouzu and Hidaka [44] suggested different active phases of CaO catalyst versus the conversion ratio. When the vegetable oil transesterification is operated in batch mode, at the low conversion ratio, either $\text{Ca}(\text{OCH}_3)_2$ produced by a reaction of CaO with methanol or the original surface of CaO cata-

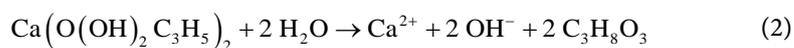
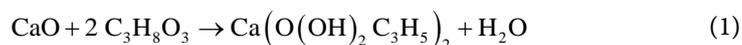
lyzes the reaction. After the conversion ratio becomes high enough to yield the appreciable amount of glycerol, CaO is transformed into $\text{Ca}(\text{O}(\text{OH})_2\text{C}_3\text{H}_5)_2$, and then $\text{CH}_3\text{O}-\text{Ca}-\text{O}(\text{OH})_2\text{C}_3\text{H}_5$ generated over $\text{Ca}(\text{O}(\text{OH})_2\text{C}_3\text{H}_5)_2$ functions as the solid base catalyst.

One interesting feature of CaO catalyst is the effect of water in the reaction system. CaO performs better in the presence of small amount of water and Liu *et al.* [48] proposed a mechanism. As a basic site of CaO catalyst, surface O^{2-} extracts H^+ from H_2O to form OH^- [1], which extracts H^+ from methanol to generate methoxide anion and H_2O [2]. When CaO is loaded in a support, the active sites remained the CaO phase. Pasupulety *et al.* [49] studied the transesterification of soybean oil over calcium oxide supported neutral Al_2O_3 ($\text{CaO}/\text{Al}_2\text{O}_3$) as solid base catalyst and they suggested that the main active phases which catalyzed the reaction are similar to those of pure CaO.

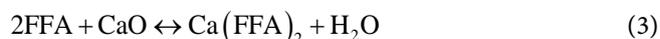
2.2. Deactivation of CaO Based Catalysts under Transesterification Reaction

The deactivation mechanism of CaO based catalysts towards transesterification can be classified into three main reasons reported by literature data: [1] leaching of active sites, [2] surface poisoning and/or pore filling and [3] [6] structural collapse.

Firstly, the leaching of active sites into the reaction medium is one of the most important reasons of CaO based catalyst deactivation suggested in literature. Kouzu *et al.* [47] [50] pointed out that some soluble substance was leached away from the CaO solid base catalyst during the transesterification reaction. CaO reacts with two molecules of the co-produced glycerol under the transesterifying condition, and then is transformed into $\text{Ca}(\text{O}(\text{OH})_2\text{C}_3\text{H}_5)_2$ (Equation (1)), which is slightly less active in the vegetable oil transesterification than CaO catalyst. The formed calcium diglyceroxide is reactive to moisture as showed in Equation (2).



CaO based catalysts are limited for biodiesel production in the transesterification reaction of crude oils, because the free fatty acid (FFA) in crude oils easily reacts with the Ca ions on the surface of the catalyst to form calcium soaps $\text{Ca}(\text{FFA})_2$ (Equation (3)), which significantly leads to deactivation of the catalyst, reduces the yield of ester and creates difficulties in the separation phase of ester and glycerol.



Furthermore, the calcium soap can detach from the surface of the catalyst and create a soap colloidal solution [51].

While the rate of CaO catalysis is accelerated in the presence of water, too much water (more than 2.8% by weight oil) in the methanol hydrolyzes fatty

acid methyl esters (FAME) to generate methanol and fatty acids, which can react with CaO to form also soap [48].

Apart from the leaching of active species, there are other reasons behind catalyst deactivation: surface poisoning and pore filling. Pore filling and adsorption of intermediates (diglyceride, monoglyceride) or products species (glycerol, FAME) led to the low accessibility of the active sites of metal oxides to the reactants, which considerably reduced the FAME yield. Furthermore, CaO is easily deactivated by carbon dioxide (CO₂) and moisture (H₂O) adsorption on the catalyst surface during handling. Soybean oil was transesterified at reflux of methanol using CaO catalyst obtained by atmospheric calcination. The yield of FAME was below 10% even at 4 h of reaction time [50]. This low yield is probably due to catalyst surface hydration (Equation (4)) and carbonation (Equation (5)).



That is why Endalew *et al.* [51] covered CaO based catalyst with glycerol in order to avoid atmospheric CO₂ contact with catalyst just after removal from the reaction mixture. The last reason of CaO based catalysts deactivation is the collapse of the layered structure [17]. Mesoporous catalysts have received a great attention for biodiesel production because these materials offer a large accessible surface area for catalyst to react [52]. However, the mesopores of CaO based catalysts can be collapsed at moderate to high temperature [6].

2.3. Analytical Approaches for CaO/MgO Based Catalyst Activity Changes Measurement

The appreciations of heterogeneous catalysts efficiency are done through the changes of the physical and chemical properties. A wide range of analytical techniques for catalysts characterization were used, but the selection depends on the information provided by the techniques. We selected here recent experimental techniques that were used during the last 10 years to describe CaO and MgO based catalysts under transesterification reaction. **Table 1** summarizes physical and chemical properties of catalysts before the first use (fresh catalyst) and after one or more uses (used catalyst).

X-Ray Diffraction (XRD) is the most widely employed technique for general crystalline material characterization because it allows the identification of crystalline phases in bulk materials and the determination of crystallite size and shape from diffraction peak characteristics [53] [54]. Liu *et al.* [55] and Li *et al.* [56] respectively investigated an activated carbide slag and calcined carbide slag waste reuse for biodiesel production from peanut and soybean oil with methanol. The activated carbide slag showed new crystalline phases, corresponding to calcium diglyceroxide. The formation of hexagonal calcium carbonate as one of the major phase was observed by XRD analysis in reused Li/CaO catalyst employed for waste cottonseed oil transesterification [57].

Table 1. Physical and chemical properties of the fresh and used CaO and MgO based catalysts in transesterification reaction.

Method	Catalyst	Fresh catalyst properties ^a	Used catalyst properties ^b	Reference
XRD	Calcium oxide	Crystalline phases of calcium oxide with 2θ values of 32° and 37°	Major crystalline phase of calcium diglyceroxide with 2θ values of $8^\circ, 10^\circ, 21^\circ, 24^\circ$ and 26°	[47]
	Calcined waste carbide slag	Dominant composition of cubic CaO with 2θ values of $32.2^\circ, 37.4^\circ, 53.8^\circ, 64.1^\circ$ and 67.4°	Appearance of new peaks of calcium diglyceroxide with 2θ values of $8^\circ, 10^\circ, 21^\circ, 24^\circ$, and 26°	[56]
	Activated carbide slag	Crystalline phases of calcium oxide	New peaks of calcium diglyceroxide units with 2θ values of $10^\circ, 21^\circ, 24^\circ$ and 26°	[55]
	Palm oil mill fly ash supported CaO	Crystalline CaO phase with high concentration of 83 wt.% ($2\theta = 32.32^\circ, 37.48^\circ, 53.95^\circ, 64.31^\circ$ and 67.47°)	Crystalline CaO phase with concentration of 56% at 5 th cycle	[58]
	Li/CaO	Major phase of cubic CaO, hexagonal Ca(OH) ₂ ($2\theta = 20.94, 37.25^\circ, 48.99^\circ, 53.70^\circ, 64.40^\circ$ and 72.2°) and minor hexagonal calcium carbonate phase ($2\theta = 21.46^\circ, 36.3^\circ, 43.3^\circ, 48.8^\circ$) with Li/CaO crystallite size of 60 nm	Structural changes with appearance of new peaks of hexagonal calcium carbonate as major phase ($2\theta = 32.3$ and 67.6) and decrease of Li/CaO crystallite size of 52 nm	[57]
	SrO/MgO	Diffraction lines of SrO, Sr and Mg carbonates and hydroxides	Roughly disappear of diffraction lines of the Sr phase (oxide, hydroxides and carbonates).	[9]
	Calcined Mg/Al hydrotalcite	Highly crystalline layered double hydroxide structure ($2\theta = 11.7^\circ, 23.2^\circ, 34.7^\circ, 38.8^\circ, 46.0^\circ, 60.6^\circ$ and 61.8°), with crystallite size of 11.2 nm	Major modification in the structure of the catalyst, with both hydrotalcite and MgO phases	[59]
	Calcined Mg/Al hydrotalcite	Mg-Al complex oxides (MgO-like or magnesia-alumina solid) phases with 2θ values of 43 and 63° , and small peaks of Al cations	Disappear of active sites due the structure collapsed	[22]
FTIR	Calcined clam shells	Prominent phase of CaO ($2\theta = 32.1, 37.4$, and 53.8°) and minor phase of Ca(OH) ₂ ($2\theta = 8.1$ and 34.2°)	Prominent phase of calcium glyceroxide with 2θ values of 8.2 and 10.1°	[53]
	Calcined waste carbide slag	Major bands of CO ₃ ²⁻ (1416 and 874 cm^{-1}), and minor bands of H ₂ O (3645 and 1648 cm^{-1}) adsorbed on the surface of the solid sample	Apparition of new bands similar to glyceroxide units : stretching vibration of C-H ($2920, 2879$, and 2849 cm^{-1}), bending modes of C-H bonds ($1470, 1448, 1425, 1265, 1231, 947$, and 916 cm^{-1}), C-O-H bending modes (1379 and 1311 cm^{-1}), and the stretching mode of C-O bonds (1132 and 1076 cm^{-1})	[56]
	Activated carbide slag	Absence of carbonate and hydroxide bands	New bands similar to calcium diglyceroxide with stretching vibration of C-O bonds ($1022 - 1083\text{ cm}^{-1}$ and $1120 - 1147\text{ cm}^{-1}$), vibration of H-C-H bonds ($705 - 1022\text{ cm}^{-1}$ and $1209 - 1346\text{ cm}^{-1}$), and weak band of O-H bonds (3643 cm^{-1}) corresponding to water	[55]
	SrO/MgO	Bands similar to Sr (1450 and 1250 cm^{-1}) and Mg carbonates and hydroxides	Disappearance of Sr hydroxide and carbonate bands	[9]
Calcined Mg/Al hydrotalcite	Non determined	Viscous liquid adsorbed on the surface of the catalyst similar to glycerol bands ($3415, 2934, 1654, 1047, 923, 851\text{ cm}^{-1}$)	[22]	

Continued

	TiO ₂ -MgO	BET surface area of 36.3 m ² ·g ⁻¹ , pore volume 0.16 cm ³ ·g ⁻¹ and average pore diameter 16.1 nm	Increase of BET surface area (42.7 m ² ·g ⁻¹), pore volume (0.21 cm ³ ·g ⁻¹), and average pore diameter (21.4 nm)	[31]
	Li/CaO	BET surface area of 1.3 m ² ·g ⁻¹	Decrease of BET surface area (0.88 m ² ·g ⁻¹)	[57]
BET	Calcined Mg-Al-Na and Mg-Al-K hydrotalcites	BET surface area of 189 m ² ·g ⁻¹ for Mg-Al-Na and 174 m ² ·g ⁻¹ for Mg-Al-K	Decrease of BET surface area (114 m ² ·g ⁻¹ for Mg-Al-Na and 63 m ² ·g ⁻¹ for Mg-Al-K)	[23]
	Palm oil mill fly ash supported CaO	BET surface area of 3.5 m ² ·g ⁻¹	Approximately the same surface area as the fresh (3.4 m ² ·g ⁻¹ at the 5th cycle)	[58]
	Calcined Mg/Al hydrotalcite	BET surface area of 83 m ² ·g ⁻¹ , pore volume 0.48 cm ³ ·g ⁻¹ and average pore diameter 122.6 Å	Constant value of BET surface area (84 m ² /g), decrease of pore volume (0.31 cm ³ /g) and increase of pore diameter (148.9 Å)	[59]
SEM	Palm oil mill fly ash supported CaO	Uniform distribution of miniature agglomerates with irregular shapes to condensed mass	Physical change with more condensed mass	[58]
	Calcined Mg/Al hydrotalcite	Uniform hexagonal platelet structure and sheet structure with smaller size of 372 nm width and 72 nm thickness	No uniform as initial one and platelet-like structure of 402 nm width and 64 nm thickness	[22]
TG/DTA	TiO ₂ -MgO	Loss of adsorbed water, decomposition of Ti(OH) ₄ (373 - 603 K) and Mg(NO ₃) ₂ (623 - 833 K); Combustion of organic derivatives with exothermic peak at 625 K	Weight loss of at 423 - 773 K with an exothermic peak at 603 K, corresponding to triglycerides and glycerol decomposition	[31]
Hammett indicator	Activated carbide slag	Basic strength of 9.8 < H ₋ < 15.0	Constant basic strength of 9.8 < H ₋ < 15.0 at the 4 th cycle	[55]
	Li/CaO	High basic strength of 15 < H ₋ < 18.4	Decrease of the basic strength (11.1 < H ₋ < 15.0)	[57]
CO ₂ -TPD	Calcined Mg/Al hydrotalcite	High total basicity (953 μmol CO ₂ ·g ⁻¹) and medium strength (432 °C)	Considerable decrease of the total basicity (441 μmol CO ₂ ·g ⁻¹) and medium strength (441 °C) at the 2 nd cycle	[59]
	Calcined Mg-Al-Na, Mg-Al-K hydrotalcites	Total desorbed amount of 355 μmol CO ₂ g ⁻¹ for Mg-Al-Na and 165 μmol CO ₂ g ⁻¹ for Mg-Al-K	Total desorbed amount of 351 μmol CO ₂ g ⁻¹ for Mg-Al-Na and 174 μmol CO ₂ g ⁻¹ for Mg-Al-K	[23]
EDS	Supported CaO	High concentration of Ca (38 wt%)	Decrease of Ca concentration (15 wt% on the catalyst at the 4 th cycle)	[58]
	SrO/MgO	High Sr/Mg atomic ratio from 0.11 to 0.6	Low Sr/Mg atomic ratio (<0.1 at the 3 rd batch)	[9]
ICP-AES	CaO-La ₂ O ₃	Concentration of 24.9 ppm for Ca and 65.3 ppm for La	Ca concentration from 22.8 ppm for 2 nd to 15.2 ppm for 3 rd use	[60]

^aPhysical and chemical properties of catalyst before the 1st use; ^bPhysical and chemical properties of catalyst after one or more uses.

A palm oil mill fly ash supported calcium oxide (CaO) catalyst was developed for crude palm oil (CPO) biodiesel production [58]. The decreases in yield after each cycle were supported by the decreasing trend shown by the CaO phase concentration determined by XRD. SrO/MgO deactivation, studied by Dias *et al.* [9], was ascribable to the Sr leaching underlined by XRD. Deng *et al.* [22] also found that the active sites of the hydrotalcite Mg/Al catalyst disappeared due to its structure collapsed.

To investigate the reason for the decrease of FAME yield, Fourier transform infrared (FTIR) spectroscopy [55] [56] were used to disclose the structure change of the used calcined and activated carbide slag catalysts during reaction. The FTIR results showed that the fresh catalyst was different from those collected after reaction. In addition to bands similar to fresh catalyst, the collected catalysts presented new bands, which could be assigned to the glyceroxide units. Deng *et al.* [22] found that the viscous liquid absorbed on the surface of the calcined hydrotalcite Mg/Al catalyst is glycerol, which deactivated the catalyst.

Scanning Electron Microscopy (SEM) is a high-resolution image of the surface of a catalyst, which provides information's concerning catalytic particle morphology and active phase homogeneity near surface regions of material. Ho *et al.* [58] reported SEM image of palm oil mill fly ash supported CaO catalyst before and after transesterification reaction. The fresh catalyst had showed uniform distribution of miniature agglomerates with irregular shapes. After reaction, the catalyst appeared to be made up of more condensed mass. The deactivated hydrotalcite Mg/Al catalyst was found to have a platelet-like structure, and not uniform as the initial calcined hydrotalcite one [22].

Brunauer-Emmett-Teller (BET) theory aims to explain the physical adsorption and desorption of nitrogen on a solid surface and serves as the basis for an important analysis technique for the measurement of the pore size distribution and specific surface area of a material. Wen *et al.* [31] investigated the regeneration of TiO₂-MgO catalyst after the fourth reuse. Interestingly, results have showed that a high FAME yield (93.8%) can be achieved for the regenerated catalyst compared with that of the fresh sample (92.3%). Moreover, the BET surface area, pore volume, and average pore diameter of the regenerated catalyst were found to be larger than those of the fresh sample. In the same way, Kaur and Ali [57] explored the reason behind the loss in catalytic activity from the fresh to reused Li/CaO catalyst. The results revealed that the BET surface area of the reused catalyst decreases compared to the fresh one. Thus, they concluded that the loss of catalytic activity could be related to the decrease of the BET surface area of the reused catalyst. Similar trend was observed with hydrotalcite Mg/Al [59], Mg-Al-Na and Mg-Al-K mixed oxides catalyst [23]. Besides, there was a decrease of pore volume and an increase of average pore diameter for the regenerated Mg/Al catalyst compared to the fresh one. Ho *et al.* [58] examined the palm oil mill fly ash supported CaO catalyst reusability from CPO biodiesel synthesis. Despite the fact that the catalytic activity of regenerated catalyst dropped, the BET surface area was not affected through recycling.

Hammett indicator method is usually used to determine the basic strength of the catalyst [5]. This method is based on the change in color of acid-base indicator such as aniline and its derivatives. Kaur and Ali [57] established that the decrease in basic strength of the catalyst is primarily responsible for the reduction of Li/CaO catalytic activity upon its repeated use. However, the basic strength of activated carbide slag for the second, third and fourth time reuse was $9.8 < H_+ < 15.0$, which indicates that the basic strength of the catalysts did not decrease with the increase of reuse number. Basicity or total basic site density over heterogeneous catalysts is the number of exposed basic sites or active centers per unit mass for transesterification. The basicity is usually shown to be closely related to the catalytic performance. Total basicity and basic strength distribution of CaO based catalysts can be also measured by temperature-programmed desorption of CO₂ (CO₂-TPD), which is based on CO₂ adsorption-desorption process. The temperature of desorption and the maximum desorbed CO₂ are illustrative of the strength and amount of basic sites, respectively [44]. The basicity of the fresh and reused Hydrotalcite Mg/Al catalyst was compared. The results revealed that the basicity of the sample decreased considerably after reuse, while the basic strength remained approximately the same. Moreover, TPD experiment (without CO₂ adsorption) with catalyst after the first cycle of reaction disclosed a large amount of carbonaceous deposits, showing that basic sites were poisoned during reaction as revealed the surface area trend [59].

Surface poisoning and pore filling may decrease the catalytic activity in the reuse process due to the low accessibility of the active sites to the reactants, which reduced the FAME yield. In order to study TiO₂-MgO catalyst surface poisoning and pore filling, Wen *et al.* [31] have exploited thermogravimetry and differential thermogravimetry analysis (TG-DTA), after the first use. The results showed that a weight loss occurred at 423 - 773 K with an exothermic peak at around 603 K. This peak corresponds to the decomposition of organic species, indicating that the pores of the catalyst are filled by organic species, such as triglycerides or/and glycerol.

Energy Dispersive X-Ray Spectroscopy (EDS) provides information's concerning chemical composition of the studied material. This data provides information on stability of catalysts through the determination of element concentrations in fresh and recycled catalysts. Ho *et al.* [58] showed that the decrease of the catalytic activity of palm oil mill fly ash supported calcium oxide in biodiesel synthesis, greatly depends to the decreasing trend shown by the Ca concentration. Dias *et al.* [9] examined SrO/MgO catalysts stability by using a same sample for several batch reactions. They found that the catalytic activity decays (after the 3rd batch) with a decrease of Sr concentration in the catalyst, which is leached into reactional mixtures.

The leaching of calcium active phase is evaluated by Taufiq-Yap *et al.* [60] with an inductively coupled plasma-atomic emission spectrometric (ICP-AES) analysis. The methanolysis reactions of fresh and regenerated CaO-La₂O₃ catalyst were compared. Ca and La concentrations in the solid mixed oxide (CaO-

La₂O₃) catalyst was determined and found to be in agreement with the obtained FAME yield. The amount of Ca in the CaO-La₂O₃ catalyst gradually decreased as the concentration decreased from 24.9, 22.8 and 15.2 ppm for fresh, second and third-use catalysts, respectively. Thus, the measurement of metal dissolution into the reaction mixture or methyl ester layer provided estimation on the stability of the catalysts and inactivity to dissolution after the reaction. Ca, Mg and Zn content from CaMgO and CaZnO catalysts were determined by ICP-AES analysis [45]. It was showed that the only minor amount of calcium, magnesium and zinc was leached out during reaction in concordance with the catalytic activity of CaMgO and CaZnO after the third cycle.

Atomic absorption spectroscopy (AAS) analysis was used to investigate the leached active species into reaction mixture by measurement of dissolved Ca, Sr and Ba concentrations in biodiesel for different experimental runs [61]. It was found that BaO had the highest residual elements detected in biodiesel with nearly 14 wt% of the catalyst leached into the biodiesel layer after the reaction. Meanwhile, CaO had the lowest solubility in biodiesel, with only 0.04% weight loss. The concentration of Ca and Mg ions leached into FAME for fresh and used catalysts were measured by Teo *et al.* [12]. For the fresh catalyst, the concentration of leached Ca and Mg ions were 8.34 and 6.24 ppm, respectively, due to the weak bonding between the isolated ions with the catalyst. On the other hand, the results demonstrated that minor amount of Ca²⁺ (1.75 ppm) and Mg²⁺ (0.33 ppm), were respectively found to leach out from used catalyst during 4th cycle of reaction.

3. Recycling Processes and Reusability Performance of CaO and MgO Based Catalysts

Ideally, a catalyst should be reused as many times as possible without any treatment. But deactivation of a used catalyst in transesterification for biodiesel production is seen by the drop in the biodiesel yield. The reusability of a catalyst could be achieved by an additional treatment for regeneration before next use. In general, after a reaction cycle, the catalyst follows two major steps: (i) separation from the reaction mixture for catalyst collection and (ii) treatment for its regeneration. The catalysts are recovered by filtration using separation funnel, centrifugation, sedimentation or decantation. In literature, various catalyst regeneration procedures were performed to investigate their reusability during successive runs with fresh reactants under the same experimental method. The general methods of catalysts regeneration, for transesterification reaction are given in **Figure 1**. Performance of reused catalysts depends on catalysts chemical composition and recycling conditions. **Tables 2-4** summarize the post-treatment processes after filtration and the performance of reused CaO and MgO based catalysts in biodiesel production, the number of catalyst reuse regarding the conversion rate of the transesterification. The data concerned various preparations of calcium oxide, magnesium oxide, mixed Mg/Ca oxides and supported ones in transesterification reaction from last ten years' literature.

3.1. Calcium and Magnesium Single Oxides

As MgO alone is fairly used as catalyst in transesterification reaction, very few data exist in literature about MgO reusability. In the opposite CaO has been used as catalyst in transesterification reaction despite the leaching problem described above. Many authors tested the reusability of commercial calcium oxide or calcium oxide obtained by calcination of natural sources. Viola *et al.* [62] found that the reutilization of the commercial CaO catalyst without regeneration, has showed a loss of efficiency with a reduction of FAME yield equal to 14% for CaO compared to SrO 22%. When Piker *et al.* [37] proposed a regeneration process of

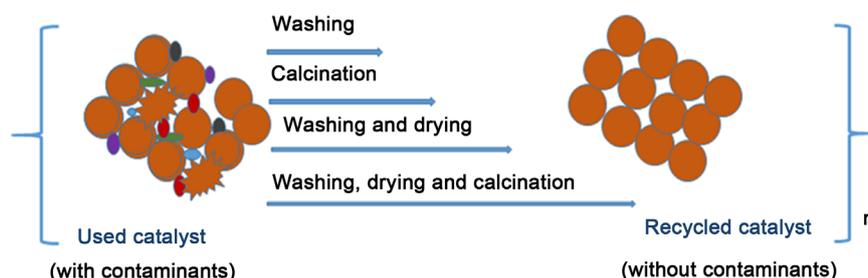


Figure 1. Regeneration methods of CaO and MgO based catalysts for transesterification reaction.

Table 2. Catalyst recycling methods, transesterification activity and number of runs and yields: Filtration without other post-treatment.

Type of oxide	FAME or FAEE yield % (1 st run to last run)	Runs number	Reference
CaO			
CaO from egg shells	95 to 75 for fresh oil	10	[37]
	93 to 62 for waste cooked oil	5	
CaO from snail shells	95 to 85	6	[40]
CaO	>90 to 70	3	[45]
CaO	Any deactivation	4	[47]
CaO from carbide slag	93.83 to 82.6	5	[55]
CaO	Reduction of 14%	2	[62]
CaO from waste fish scales	98 with no deactivation	6	[66]
CaO from clam shell	>98	2	[84]
CaO microcrystallin	90 to 80	4	[85]
Mixed or supported oxides			
CaO/ZnO	90	4	[14]
CaO/ZnO	64 to 40 for ethanolysis	>3	[15]
CaO/silicate	100	2	[19]
CaMgO CaZnO	80 for palm oil 70 for jatropa oil	3	[45]
CaO/Mg/Al	85 to 80	5	[78]
CaO-loaded microcapsules	95.5 to 80.9	4	[83]

Table 3. Catalyst recycling methods transesterification activity and number of runs and yields: Regeneration by washing and drying temperature lower to 200 °C.

Type of oxide	Regeneration process after filtration Solvent (number of washing), Temperature of drying (duration)	FAME or FAEE yield % (1 st run to last run)	Runs number	Reference
CaO				
CaO	Hexane, MeOH	>85 to 50	6	[11]
CaO	MeOH, 80 °C	83 to 65	3	[47]
CaO	Unwashed MeOH (3)	84.5 to 68.7 82.7 to 76.7	3	[63]
CaO derivated egg shell	MeOH, tetrahydrofuran, 50 °C (overnight)	>80	8	[86]
Mixed or supported oxides				
Nano Ca-Mg-Al oxide	High-speed Centrifugation, washing to 4 th reuse, EtOH	95 - 90.4 - 89.1 - 80.7 - 43.7	1-2-3-8-9	[22]
CaO/MgFe ₂ O ₄	External magnetic stirring, MeOH, 60 °C under vacuum (10 h)	>89	3	[24]
KF/CaO-Fe ₃ O ₄	Anhydrous MeOH, 105 °C	>90, reduced about 10 wt%	14	[26]
KF/CaO-MgO	Centrifugation, EtOH, dried	97.9 to 86.7	4	[28]
KF/Ca-Al hydrotalcite	Cyclohexane	95	2	[29]
MgO TiO ₂	Centrifugation, MeOH, 120 °C	92.3 - 81.2	4	[31]
CaO + Fe ₂ (SO ₄) ₃ , Li-CaO + Fe ₂ (SO ₄) ₃	Covered with glycerol	100 to 80	3	[51]
CaO Al composite	MeOH, dried	87	7	[54]
CaO from carbide slag SiO ₂ , Al ₂ O ₃	Hexane, MeOH, 100 °C (overnight)	>80	3	[56]
Li/CaO	Hexane, dried, 120 °C	98 to 84	4	[57]
CaO-La ₂ O ₃	MeOH, calcination or mixture MeOH + NH ₃ and dried (overnight)	82 with no change	2	[60]
Dolomite	Filtration under vacuum, MeOH (2), 100 °C (1 h)	98.8 to 80.97 for canola oil 96. to 84.5 for sunflower	3	[68]
Dolomite	Mixed with methanol in a reactor, ultrasonically irradiated (15 min)	96.5 to 89.5 97.1 to 88.7 (for CaO)	4	[69]
Mg ₂ CoAl	110 °C (overnight)	>90	7	[72]
Ca-doped Ce oxide	n-Hexane, 120 °C	85	15	[74]
CaO-MgO (8:2)/Al ₂ O ₃	Filtration, EtOH, dried	90 with slight decrease	4	[76]
Mg-Al mixed oxides	MeOH	>91	5	[77]
LiNO ₃ /MgO, LiNO ₃ /CaO NaNO ₃ CaO, KNO ₃ /CaO	MeOH, 60 °C (3 h)	>90 stable		[87]
Zn/MgO	n-hexane, MeOH, 110 °C	>84%	5	[89]
MgZnAl oxides (Al ₂ O ₃ /MgZnO)	Hexane, dried (12 h)	Drop of 5%	5	[90]
MgSil-org, 3MgO-4SiO ₂ -2H ₂ O	Centrifugation, MeOH	93 - 92	5	[92]

Table 4. Catalyst recycling methods transesterification activity and number of runs and yields: Regeneration with a step of calcinations.

Type of oxide	Regeneration process after filtration Solvent (number of washing), temperature of drying or calcination (duration)	FAME or FAEE yield % (1 st run to last run)	Runs number	Reference
CaO				
CaO graphite oxide	500 °C	>90 with no significant loss	4	[25]
CaO from mud clam shells	Centrifugation, n-hexane, 900 °C	96.7 to 74.5	5	[38]
CaO	MeOH, dried, 850 °C	89 to 85	5	[39]
CaO	MeOH , 850 °C (2 h)	79.7 to 60.7	3	[58]
CaO used under ultrasonic cavitation	Centrifugation, MeOH, hexane, 500 °C (3 h)	50 to 40	3	[61]
CaO rich catalyst	Acetone, EtOH, 120 °C (overnight), 600 °C - 800 °C (4 h)	75 to 50	4	[64]
CaO from waste cokle shells	MeOH, n-hexane , 900 °C (2 h)	>97	3	[65]
Mixed or supported oxides				
Sr/Mg = 0.20	750 °C under N ₂ atmosphere	96.8 to 65	3	[9]
CaMgO	Hexane, MeOH, 800 °C (3 h)	>80	4	[11]
CaZnO	Hexane, MeOH, dried in oven (overnight), 800 °C (3 h)	80 with slight decrease	6	[11]
CaO-CeO ₂	MeOH (3), 120 °C (5 h), 750 °C under He/O ₂ : 9/1	83 91	5	[13]
Zr/CaO	Hexane, 700 °C	99 to 80 to 40	1-3-4	[16]
Calcium silicate	600 °C (6 h)	100 to 90 to 70	1-3-8	[20]
K/LaMgO	MeOH, 550 °C	94 to 87	3	[30]
Hydrotalcite (Mg+Al)	MeOH (3), 200 °C (18 h)	90 to 60	3	[59]
Mg _{1-x} Zn _{1+x} O ₂ (A-FR)	MeOH, 100 °C (48 h), Dried, 461 °C (4 h 25)	78 to 68 78 to 77	4	[71]
CaO-NiO and CaO-Nd ₂ O ₃	MeOH and hexane, 900 °C (3 h)	>80	6	[73]
CaMnOx	550 °C under O ₂ and 750 °C under N ₂	>90 with slight change	6	[75]
K doped MgO	MeOH, 700 °C(3 h) in air	>95	2	[79]
KF (40%)/bentonite catalyst	MeOH (several times), 500 °C (3 h)	98.2 to 93.3	5	[81]
KF/CaO	EtOH, 560 °C under air (10 h)	>90 with no apparent loss	14	[82]
K-pumise (CaO natural pumise)	EtOH, dried, 560 °C (10 h), new ionic exchange with KOH, 120 °C (3 h)	90 with no change	6	[88]
MgO-CaO/SiO ₂	600 °C under N ₂ flow	90.1 to 88.7	3	[91]

CaO catalyst. After each reaction, the catalyst was separated by centrifugation and used again without any additional treatment (with residues of glycerol). The catalyst can be reused for ten times with fresh oil. After 9th recycling of the catalyst, the FAME yield decreased from 95 to 75 wt% and five times with waste cooked oil (WCO) (after 4th recycling, the FAME yield decreased from 93 to 62 wt%). The difference between the number of cycles that the catalyst can be reused with fresh and waste oils can be explained by the fact that FFA present in

WCO destroy the catalytic activity of CaO more quickly than that of fresh oil. Madhu *et al.* [39] prepared CaO catalyst from crab shells and tested their reuse in two ways. Firstly, the used catalyst was washed with methanol, calcined at 850°C and reused up to five times with a minor decrease of the biodiesel yield (from 89% to 84%). Secondly, the used catalyst was washed with methanol, and reused without calcination up to five times. In this case, the reused catalyst gave lower biodiesel yield compared to the first run. Poosumas *et al.* [63] showed that unwashed calcium oxide catalyst is more practical in the industrial scale is more efficient than washed with methanol. The biodiesel yields observed at 4 h for unwashed catalyst was still high at the third cycle with 76.7% against 68.7% for washed catalyst by methanol. Mootabadi *et al.* [61] proposed to selected low heating rate of catalyst to avoid the coke formation on catalyst or its sintering. After the transesterification reaction, the catalysts were separated by centrifugation, washed with methanol and n-hexane to remove glycerin and any undesired materials attached on the surface. The catalyst was then calcined in a furnace at 500°C for 3 h. The CaO catalyst was the poorest catalyst compared to BaO but underwent relatively less severe activity drop in the catalyst reusability test during three runs. Calcined palm oil mill fly ash supported CaO catalysts was prepared by Ho *et al.* [58]. After each transesterification cycle, the catalyst was regenerated using methanol washing followed by recalcination at the optimal temperature used for catalyst preparation (850°C) for 2 h. The regenerated catalyst was active for three consecutive cycles whereby the yield fell from 79.76% to 60.75%. Calcium oxide prepared from Mud clam shell and used in catalysis for transesterification of castor oil showed a slight decrease of biodiesel yield after five cycles with a decrement of 12.2% [38]. In the reactivation procedure used by Luque *et al.* [64] for carbonaceous ash-like residue upon reaction completion, the catalyst was filtered off, washed thoroughly with acetone and ethanol and dried at 120°C overnight prior calcination at 600°C - 800°C (4 h). These materials showed a significant decrease in activity after the second use. Subsequent reuses and reactivation cycles gave similar results, pointing out a partial deactivation of the catalyst, which in any case could provide a 50% conversion to FAME after four reuses/reactivation cycles. Boey *et al.* [65] reported the use of waste coke shells as a source of calcium oxide for transesterification. Reusability results confirmed that the prepared catalyst could be reused up to three times under the optimized conditions (4.9 wt% catalyst and 0.54:1 methanol/oil mass ratio) with a yield above 97%. Before reuse, the spent catalyst was washed with methanol and n-hexane and calcined at 900°C for 2 h. CaO derived from waste Rohu fish was reported by Chakraborty *et al.* [66] as a very effective catalyst for transesterification for a FAME yield 97% - 98%. To prepared the catalyst, waste fish scales were washed with hot distilled water several times, drying in hot air oven at 100°C for about 6 h, ground to fine powder, calcined at temperatures between 600°C - 1000°C for 2 h. This prepared catalyst was found to be chemically stable as it could demonstrate retention of catalytic activity over 5 h reaction time for consecutive six experimental runs without remarkable deactivation.

Sánchez-Cantú *et al.* [67] evaluated CaO as solid base catalysts in the transesterification of castor oil and methanol. After the first use a 100% conversion was detected. After 3 cycle catalytic activity simultaneous leaching of $\text{Ca}(\text{OH})_2$ and calcium diglyceride (main cristaline phase) were observed. However, an important decrease of conversion was observed in the first reuse (63% conversion), followed by an increase to 88% and 84% after the second and third reuse, respectively.

3.2. Binary Oxides: CaO/MgO

Correia *et al.*, [68] studied the dolomite catalyst calcined at 850 °C for 3 h during three cycles of reaction. In each cycle, the catalyst was separated from reaction medium, using a vacuum system, washed twice with methanol and dried at 100 °C for 1 h. This catalyst showed a slight decrease of the catalytic activity after each reuse. The yield in FAME decreased from 98.81 for first cycle to 80.97% for third cycle, due to the high leaching of metal oxide. Korkut and Bayramoglu [69] presented one quick method of catalyst regeneration. Catalyst prepared from dolomite was recovered by filtration at the end of the first reaction, mixed with methanol, poured in the reactor and was ultrasonically irradiated for 15 min. To compensate the catalyst lost during the washing and filtration steps, 5% fresh catalyst was added into the ultrasonic reactor. Then, the predetermined amount of oil was added and the reaction was restarted. In this case, dolomite can be reused four times in transesterification reaction with a loss of 7% biodiesel yield when CaO gave 8.4% biodiesel yield loss.

3.3. CaO and MgO Mixed with Other Metal Oxides

Calcium and magnesium are usually prepared with other metals (Zn, Fe, Co) as oxides. The preparation could be a co-precipitation process to form a mixed oxide. Also in biodiesel production, CaO and MgO could be supported by silica and alumina for potential heterogeneous catalyst.

Calcined calcium zincate [15] as catalyst for the methanolysis of sunflower oil, was reutilized during three catalytic runs, with FAME yields higher than 85 wt%. This stability was attributed to the strong interaction of calcium oxide with zinc oxide in the structure of the catalyst. When the same catalyst was used with ethanol, a progressive deactivation was observed. Fatty acid ethyl esters (FAEE) yield was lower than 40 wt%, after the third cycle. The authors suggested as cause of the catalyst deactivation in the ethanolysis process, the properties of ethanol as solvent, which provokes the progressive lixiviation of the catalyst.

Kesic *et al.* [14], showed that the CaO-ZnO catalysts were practically insoluble in methanol indicating that CaO properties are improved by the mixing with ZnO. After four runs, the biodiesel yield reached 90% without any treatment of the catalyst.

Ngamcharussrivichai *et al.* [70] prepared Ca-Zn mixed oxides (CaO-ZnO) by co-precipitation. When the amount of Zn increases or Na_2CO_3 is added as co-precipitant in the mixed oxide, the activity of the catalyst was enhanced and

the biodiesel yield reached 94.2% at 800°C. Reuse of the catalyst gave yield above 90% up to three times after washing with methanol and 5 M ammonium hydroxide and drying. Olutoye and Hameed [71] prepared Al₂O₃ modified MgZnO. The reusability of the MgZnAlO solid catalyst, which represents its capacity to perform the same catalytic activity, was evaluated by conducting several experimental runs after the first batch at the optimum conditions obtained for the FAME yield. The catalyst after the first reaction was recovered, washed with n-hexane to remove oil residue adhered to the surface of the catalyst and dried for 12 h. The catalyst was then used for five consecutive runs to obtain FAME. A selected La-Mg mixed oxide catalyst [30] was checked for reusability and it showed conversion yields of 94%, 90% and 87% during the first, second and third cycles respectively. Liu *et al.* [24] explored the recyclability of the magnetic CaO/MgFe₂O₄ catalyst. The transesterification reaction was carried out five times and the yield of FAME could remain above 89%. Endalew *et al.* [51] explored solid CaO + Fe₂(SO₄)₃ and Li-CaO + Fe₂(SO₄)₃ catalysts which catalyzed simultaneously esterification and transesterification of *Jatropha curcas* oil with FFA content in a single step. Reuse performance of CaO/ Fe₂(SO₄)₃ catalyst, showed that first run yield and second run yield are the same but a decrease is observed for the third run. The catalyst was after each use, covered with glycerol to avoid air contact and so deactivation by CO₂ and moisture. This simple method is efficient than a second method of recycling by drying the catalyst at 250°C to burn the residual biodiesel and keep the glycerol below the boiling point. Li *et al.* [72] incorporated cobalt and lanthanum into the mixed oxides in order to prepared mixed oxide catalysts derived from Mg-Co-Al-La layered double hydroxide (LDH). This promote the formation of spinel phase but turned into a gel-like substance during transesterification reaction that would stabilize the catalyst during the application and to avoid that the catalyst turned into a gel-like substance during transesterification reaction. The active mixed oxide catalyst Mg₂CoAl in the transesterification of canola oil with ethanol was recycled after collection from the reaction mixture through filtration. The collected catalyst was dried overnight at 383 K and stored in a desiccator without any further treatment. The catalyst showed no reduction in activity over seven reaction cycles as the FAEE yield is very similar to that of the initial unused Mg₂CoAl. Taufiq-Yap *et al.* [60] synthesized Ca/La oxide catalysts and tested three procedures to generate the spent catalysts obtained from the first run. The washing with methanol followed by calcination and the washing with a mixture of methanol and ammonium solution and dried in oven for overnight achieved the same high FAME than the fresh catalyst, with biodiesel yields production more than 82%. Teo *et al.* [73] studied three catalysts (CaO-NiO, CaO-Nd₂O₃ and CaO) for reusability test. After completion of each run, the use catalyst was separated from the reaction mixture and washed several times with methanol and n-heptane solvents simultaneously. The solid particles collected were calcined at high temperature of 900°C for 3 h. When the CaO-NiO and CaO-Nd₂O₃ catalysts were reused for sixth cycles, the FAME yield was maintained

above 80% without remarkable decreased. In Wen *et al.* [31] studies, TiO₂-MgO mixed oxides were centrifuged from the reaction mixture, washed with methanol (four times) to reduce the effect of surface poisoning, pore-filling, and the dried at 393 K. After the forth reuse, the catalysts were calcined. As the efficiency of reuse depends on washing methods, a two-step washing method was applied. After the catalyst separation, it was washed with methanol four times and subsequently with n-hexane once before being dried at 120°C. The biodiesel yields obtained by two-step method were higher than those recycled only by methanol washing. A higher FAME yield (93.8%) could be achieved for the regenerated catalyst compared with the fresh sample (92.3%). The FAME yield decreased slowly to 81.2% when this process was repeated four times. To test the reusability of Zr/CaO catalyst, Kaur and Ali [16] performed transesterification of the jatropha oil with methanol under optimized reaction conditions. After the completion of the reaction, Zr/CaO catalyst was recovered from the reaction mixture by filtration, washed with hexane and finally regenerated at 700°C as calcination temperature. The regenerated catalyst was employed for four successive catalytic cycles under the same experimental and this regeneration method was found to yield 99% FAME in the second run.

For a mixed Li/CaO, the recovered catalyst was washed with hexane and finally dried at 120°C [57]. This catalyst was able to yield 98%, 90% and 84% conversion of waste oil into corresponding FAEE in first, second, and third catalytic run.

Thitsartarn *et al.* [74] prepared a Ca/Ce oxide catalyst which can be reused up to 15 cycles with the retained catalytic performance. After each reaction cycle, the catalyst was separated from the liquid product by filtration, washed with n-hexane to clean up the catalyst's surface, dried at 120°C and reused for the next reaction cycle without recalcination. The biodiesel product contained extremely low amount of catalyst components leached out from the catalyst (*i.e.* <1 ppm after the 7th cycle).

When catalysts based CaMnO_x prepared by Dias *et al.* [75] were reused, they were first heated at 550°C in a tubular furnace under O₂ atmosphere to ensure complete removal of organics and further activated by calcination at 750°C under N₂ atmosphere. No loss of activity occurred in the first run, while a small decrease of the activity was observed in the sixth run.

3.4. Supported CaO and MgO Catalysts

Hsin *et al.* [20] prepared Mesoporous Calcium Containing Silicate (PMCS) catalysts. All catalysts studied could be reused for eight times with similar reactivity after regenerated by calcination at 600°C for 6 h. But when the catalyst was collected by direct filtration and lypholization, it did not yield good recyclability (50% yield at 2 h for the second cycle). Using CaO-MgO/Al₂O₃, Mahdavi and Monajemi [76] found that cottonseed oil conversion was over 90% and the (12.5 wt%) CaO-MgO (8:2)/Al₂O₃ catalyst maintained activity even after being used for four cycles. The catalyst was recycled by washing with ethanol and dried.

One other example comes from Silva *et al.* study [59] with Mg-Al hydrotalcite catalysts. Washing with methanol and reheating at 200°C did not recover the hydrotalcite (Mg/Al oxide) structure and the FAME yield decreased from 90 to 60% at second and third cycle. Wang *et al.* [54] study a solid Ca/Al composite oxide based catalyst containing $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and CaO and applied it to transesterification of rapeseed oil with methanol. The results revealed that the catalyst is easily separated from the reaction mixture, as it is insoluble in methanol. When calcined by 1000°C, the catalyst could be reused for at least seven cycles with FAME yields maintained above 87%. After reaction, a nano Ca-Mg-Al oxide catalyst was separated by high-speed centrifugation, and reused [22]. Biodiesel yield was decreased from 95% for *Jatropha* oil to 80.7% for third time. On the other hand, the catalyst was separated, the viscous liquid absorbed on the surface of the catalyst was removed by washing with ethanol, and the catalyst was reused. At the 8th time reused, biodiesel yield was 89.1% but at the 9th time, biodiesel yield sharply decreased to about 43.7%. In another study Zeng *et al.* [77] observed that Mg-Al mixed oxides prepared by urea method were stable at least for five cycles. The biodiesel yield kept over 91% when the catalyst was washed with methanol. The reusability of Ca/MgAl oxide in five consecutive runs without expressive loss in the activity [78] were examined. For that after each reaction, the solid was centrifuged and the supernatant solution was removed. Teixeira *et al.* [79] investigated the reusability of the K-doped MgO catalyst by washing the used catalyst with methanol and calcining at 700°C. The results showed that the catalyst could be reused for three times without any significant decrease of the activity. Direct reuse of the catalyst (without thermal treatment at 700°C) showed very low conversions.

Graphite oxide (GO) supported CaO [80] was successfully applied to the transesterification of soybean oil with methanol. The catalyst maintained high activity (>90%) and could be reused after calcination at 500°C up to four consecutive reaction cycles with no significant loss of activity after four cycles. Therefore, Fan *et al.* [28] concluded that KF/CaO-MgO catalyst not only exhibits a favorable catalytic performance during the transesterification reaction but also has perfect reusability by a decrease of FAME yield from 97.9% to 86.7% at the fourth run. A relatively small 5% loss of activity was observed by Boz *et al.* [81] at the end of third reuse of the KF (40%)/bentonite catalyst when the catalyst was washed several times with methanol, and re-calcined at 773 K for 3 h. The prepared KF/CaO [82] can be reused for 16 times with no apparent loss of activity in batch process. And this deactivated catalyst can be regenerated just by calcination in air. That is a simpler operational procedure, and generates less pollution. Nano-magnetic solid base catalyst KF/CaO- Fe_3O_4 was synthesized by Hu *et al.* [26] and used as catalyst for transesterification. The catalyst, after 3 h transesterification, was separated by a permanent magnet. Then it was washed with anhydrous methanol and dried at 105°C. It was found that the catalyst maintains sustained catalytic activity even after being reused for 14 times and the catalyst is reduced about 10 wt%. After 16 times of reuse, however, the catalyst loses activ-

ity seriously. CaO-loaded microcapsules were filtered with an open mesh and reused in a new reaction cycle without any treatment [83]. The FAME yields at 4 h obtained from 1st, 2nd, 3rd, and 4th cycles were 95.5%, 97.7%, 94.5% and 80.9%.

4. Summary, Performance of Recycling Processes and Challenges

4.1. Summary

The use of catalyst in transesterification reaction is limited by the decline in activity with repeated uses. Activity of a catalyst in transesterification reaction and the changes in this activity were explored and the mechanism suggested in the literature for CaO catalyst. The active phase of CaO catalyst in transesterification involves the oxygen anion present on the CaO surface, and nucleophilic compounds such as $\text{Ca}(\text{OCH}_3)_2$ and $\text{Ca}(\text{O}(\text{OH})_2\text{C}_3\text{H}_5)_2$, formed *in situ* in the reaction mixture. Small amount of water was found to be beneficial in the reaction system. The deactivation mechanism of CaO based catalysts towards transesterification is demonstrated to be due mainly to partial dissolution of catalyst in the reaction mixture and the poisoning of the catalyst active sites.

A wide range of analytical techniques was used to describe CaO and MgO based catalysts deactivation. FTIR spectroscopy was used to show new bands, assigned to the glyceroxide units. The XRD profile showed crystalline phases variation, eventual collapse, evolution of active phase concentration (CaO, calcium methoxide and calcium diglyceroxide) and surface poisoning (carbonation and hydration) of catalysts during reuse. SEM showed the uniformity of material, irregular shapes or a platelet-like structure. The BET showed that the loss in catalytic activity could be related in many cases to the decrease of the BET surface area of the reused catalyst, a decrease of pore volume and an increase of average pore diameter. The basic strength of the catalysts varied from considerably decrease to no change with the increase of reuse number. The TG-DTA showed the decomposition of organic species, indicating that the pores of the catalyst are filled by organic species, such as triglycerides and glycerol.

Calcium oxides, magnesium oxides, their mixed or supported oxides represent interesting materials among heterogeneous catalysts for transesterification in term of reusability. When separated from the reaction mixture by filtration, the catalyst could be reused without any treatment or recycled by washing, drying or/and recalcination. The reusability of a catalyst depends on regeneration methods to ensure complete removal of organics poisoning surface of catalyst. The collection of the catalyst from the reaction mixture is usually done through simple filtration. Most cited solvents used for washing are methanol, ethanol and hexane. Next step in a catalyst regeneration process is drying, followed or not by calcination at temperature range from 100°C to 900°C. Results showed that the solvent washing and drying or calcination processes used by most authors for the catalysts regeneration do not recover the initial catalytic efficiency of the catalysts. This implies that the leaching phenomenon could be the main reason that deactivates the catalysts during the cycles.

From the literature data, we considered that a catalyst used after multiple runs is efficient when it reaches 90% of FAME production. CaO and MgO solid based catalysts from natural resources or not, in most cases (Tables 2-4), could be reused many times as catalyst for biodiesel production without rigorous treatment. However, involving other elements such as Al, Si, Ce, Co, Zn, Fe, Ni, Nd, Ti, Zr, Mn, Li, Sr, K and F, better catalyst reusability could be obtained in the biodiesel production. These catalysts showed less leaching and performed FAME or FAEE yield >90% with many reaction runs when reactivated by washing with solvent and calcinated at different temperatures. Few examples of CaO and MgO supported graphite or prepared as nanoparticules present also reusability capacity.

4.2. Performance of Recycling Processes

CaO and MgO based catalysts, single [84] [85] [86], doped [87] [88], mixed [89] [90] or supported [91] [92] have allowed much attention in recent years due to their excellent catalytic performance, however these catalysts generally show a limited recyclability (less than 10). One can find in literature the example of a high number of reuses for a catalyst in transesterification reaction. The based starch catalyst reported by Lou *et al.* [93] showed excellent stability as it gives good yields in transesterification and could be reused during 50 cycles in successive reactions. Yan *et al.* [94] reported that the Zn_3La_1 catalyst they prepared was recycled 17 times in a batch reactor without loss of activity and maintained a high FAME yield (92.3%) for 70 days in a continuous tubular flow reactor. In comparison CaO and MgO based catalysts showed a high number of reuse potentiality as above 16 uses with Ca/Ce oxide [74]. Mixed KF/CaO could be a very attractive heterogeneous catalyst with repeatability for 16 cycles to achieve biodiesel yield 97% - 91% [82]. Hu *et al.* [26] used KF/CaO- Fe_3O_4 catalyst for 14 times in transesterification reaction. All these experiences show that other elements incorporated in CaO or MgO catalyst play an important role in the catalyst stability by reducing its leaching and prolonging the lifetime. Incorporation of CaO or MgO in a support framework like ZnO [11] [14] [15] effectively reduces the leaching of the catalyst and maintain its activity. Taufiq *et al.* [11] studied pure CaO, dual CaO/MgO or mixed with Ca-Mg-Zn oxide. The last one mixed with Zn, is the more stable. These results suggest that the CaO, MgO catalyst based catalyst are promising catalysts for long-term usage for the effective production of alternative biofuel with environmental-benign process.

4.3. Challenges on Catalyst Reusability in Biodiesel Production

To ensure an economically viable synthesis of biodiesel by reducing the cost of production, [95] and for real application to large-scale or industrial scale an important characteristic feature of a catalyst is its “reuse” property. This reusability of prepared catalyst is a challenge to make the biodiesel production more economical. During recycling, it is also important to avoid negative aspects: toxic solvent use, energy consumption and operational constraints to achieve the goal

of resources recovery in green chemistry for a sustainable development. These limitations could be mitigated through appropriate choice of preparation and recycling conditions of catalysts. Literature data showed that calcium oxide and magnesium oxide based catalysts, are successfully used as catalyst for biodiesel development. In addition, there are available in nature, resistance to atmospheric poisoning, and were found to be cost effective.

A continuous-flow production of transesterification process using solid catalyst with good stability without any treatment is obvious economic [14] [37] [40] [62] [78]. The long lifetime of the catalyst contributes to decreasing the cost of biodiesel production due to good stability. Before the selection of catalyst, there is a need to evaluate the reusability through the feasibility, the cost and the impact in environment compared to a fresh catalyst preparation.

In the case of catalyst poisoning, the regeneration process by a good washing (one time or several times with a solvent) could be applied to reverse the deactivation. A great number of solvents are possible to use to eliminate any organic residues over the catalyst surface: polar molecules as glycerol, soap and less or non-polar compounds: biodiesel, triglycerides (TG), partial reacted oil: *i.e.* diglyceride (DG) and monoglyceride (MG). The most cited is methanol used as alcohol in the transesterification reaction. Many others are used ethanol, hexane, heptane, cyclohexane, THF, butanol, acetone to remove organic contaminants. The washing by eliminating organic pollutants helps to reduce the temperature of catalyst calcination at the high temperature. All these washing solvents generated pollution. Only in the case of CaO-ZnO catalyst prepared by Ngamcharusrivichai *et al.* [70], ammonium hydroxide is used to wash the catalyst. Sometimes two steps were used to take profit and increase the number of runs of the catalyst [57].

More dramatic is the catalyst-leaching problem, which increases the operational cost due to the need to purify the biodiesel. Crude biodiesel produced by alkali-catalyzed transesterification must be refined to fulfill the biodiesel standard specifications for commercial use and this additional step leads to wastes production.

To reduce cost of biodiesel, bioethanol and recycled oil as cheapest raw materials, were seen as promising alternatives in the production of biodiesel. As the FFA deactivates catalysts due to leaching, this affects the reusability, and reduces biodiesel yield for oil rich in free fatty acids and for esterification of FFA [37]. This alternative could be seen as limitation to the lifetime of catalyst. When Rubio-Caballero *et al.* [15] studied calcium zincate for methanolysis and ethanolysis of sunflower oil. A progressive deactivation in ethanolysis was observed and the authors suggested that ethanol as solvent, provokes the lixiviation of the catalyst. But for ethanolysis, we note good yield of FAEE and reusability of Li/CaO [72] and Mg-Co-Al-La [57] catalysts recycled with reasonable temperature (200°C).

Also the organic contaminants or water can be eliminated from a used catalyst effectively by thermal treatment (drying, calcination at different temperatures)

with or without washing. In the context of energy analysis to determine the net advantage of reuse of solid catalysts for industrial application must be evaluated. Recalcination of catalyst to burn away deposited or adsorbed organic compounds before each reuse is an energetivores condition in recycling. Madhu *et al.* [39] showed the importance of regeneration temperature of CaO catalyst from crab shells. After their study, they concluded that calcination at 850°C after treatment with methanol, renders activated the catalytic sites of CaO catalyst and maintains the yield of biodiesel during five reuses. We note in **Table 4** that high temperatures (>900°C) are needed for some catalysts regeneration [38] [58] [65] [66] [71] [73] [79].

5. Conclusion

A great variety of Ca and Mg oxides mixed or supported were prepared and used as catalysts in transestefication reaction for biodiesel production. Activation theories supported by physico-chemical analysis explain changes in catalysts during reaction and regeneration processes. This paper describes the gradual decrease of CaO and MgO based catalysts activity during reuse. Heterogeneous CaO and MgO based catalysts are efficient as they could be provided from natural sources and they showed high reactivity in transesterification reaction. In addition, a strong interaction of CaO and MgO with other oxides prevents lixiviation and gives high stabilization to the catalyst during transesterification reaction. As reusability is not linked to the origin of CaO or MgO oxides, CaO catalyst from egg shells was reused 10 times with good yields in transesterification reaction without recycling process. This protocol could be cited as easier to apply in biodiesel production. To increase the stability of the catalyst and the reused number, the selection of a mixture CaO/ZnO or KF doped CaO-MgO presents advantages to be reused many times without washing with toxic solvent and high thermal treatment. KF doped CaO-MgO or CaO-Fe₃O₄ catalysts exhibit favorable catalytic performance during transesterification reaction and have perfect reusability for 14 times. Thus, the development of new stable and active class of solid oxides based CaO or MgO as recyclable catalysts must integrate a mixture of oxides. One further sustainable approach for biodiesel production with recycled catalyst, in addition to cost minimization, is to avoid high energy and toxic washing solvent consumption.

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Author Contributions

Mr. Nombamba Oueda designed the introduction, Dr. Igor W. K. Ouédraogo wrote the mechanistically approach section and Prof. Yvonne Bonzi Coulibaly

wrote the recycling processes. All authors participated to the finalization of sections of the manuscript during discussion meetings by individual contribution.

Conflicts of Interest

The authors declare no conflict of interest.

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