Nanocatalyst for Biofuel Production: A Review

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Abstract The demand for renewable and alternative types of energy has taken a new dimension; the primary reason is traceable to the climate change effects that fossil-based fuels have in the earth atmosphere. Bioenergy is one of the many arrays of renewable forms of energy that have taken centre stage in replacing the conventional fossil-based energy sources. Biofuel is the liquid or gaseous fuel derived from biological processes such as agriculture (biomass) or anaerobic digestion (solid or liquid wastes) or a combination of both, rather than geological processes that are known with the traditional fossil-based counterparts. Biomass energy is readily available and environmentally friendly, because it does not lead to a net increase in carbon dioxide levels and produces low amounts of sulphur. An effective implementation of biomass in the current energy scheme would involve the development of new technologies for the large-scale production of biofuel. The two primary methods for converting biomass to biofuels are thermochemical and biochemical processes. Thermochemical conversion is a major path for producing products such as bioethanol, biodiesel, bio-oil, bio-syngas and biohydrogen. It includes fast pyrolysis, liquefaction, combustion and gasification. Liquefaction of biomass to bio-oils involves two main routes which are hydrothermal and catalytic liquefaction. Catalytic liquefaction is very similar to hydrothermal liquefaction; however, a catalyst is used to reduce the residence time, operating temperature and pressure thereby increasing the quality of liquid products. Thermochemical biofuels are getting much more attention lately as these biofuels offer several technical and strategic advantages, such as highly developed industrial infrastructure and the biofuels can be produced from virtually all sorts of available biomass in a reasonable timeframe without significant modification in the overall process. At lower reaction temperatures, thermal processing of biomass with catalytic methods offers the possibility of selectively yielding a narrow range of products and reducing the energy requirements of the transformations. In terms of catalysts used, for biodiesel production, heterogeneous catalysts in comparison to homogeneous catalysts

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N. Srivastava et al. (eds.), *Green Nanotechnology for Biofuel Production*, Biofuel and Biorefinery Technologies 5,
https://doi.org/10.1007/978-3-319-75052-1_4

provide more effective separation steps for products and catalysts, eliminate quenching process, and offer conditions for the continuous production process. The objective of this review is to discuss the trends, recent advances in heterogeneous catalysts and expected contribution to knowledge, specifically in nanocatalysts for biofuel production, such as metal oxide catalysts (e.g. ZnO), metal supported by metal oxide catalysts (e.g. Au–ZnO), Alloy (e.g. Cu–Co), Metal oxide supported by metal oxide (e.g. KF–CaO–Fe_3O_4). Our focus will be on heterogeneous catalysts.

Keywords Renewable energy · Biodiesel production · Biomass Thermochemical processes · Catalysis · Nanocatalysts · Heterogeneous catalysts

1 Introduction

Availability of cost-effective and reliable energy sources is considered one of the important characteristic of modern society. Unfortunately, most of the societies in the world continues to rely heavily on fossil fuels such as oil, natural gas and coal. The production of fossil fuels have a significant societal and environmental impact varied from production to utilization which affects water, air and earth temperature that leads to global climate change. Alternative energy sources such as nuclear and renewable energy (wind, solar and biomass) can offer new cost-effective solutions to the energy production. These sources can increase the energy efficiency and help to reduce the environmental impacts.

The world energy demand has continued to take an upward trend. The primary reason for this increase is not unconnected with the world population and our methods of energy consumption. Despite the recent reduction in crude oil prices, fossil-based fuels remain energy sources that must eventually be replaced worldwide due to the diminishing fossil fuel reserves along with climate change effects caused due to constantly increasing levels of greenhouse gases in the earth atmosphere (Matthews et al. 2016). Bioenergy has been touted as one of the best alternative sources of energy to replace fossil-based fuels eventually. Biofuel is the term denoted to liquid or gaseous fuels derived from biomass, and a transition from fossil-based fuels to biofuels is assumed to reduce emissions of climatic gases (Berg 2013). The primary alternative sources of energy systems that can replace fossil fuels are water, wind, solar energy and biomass. Biomass energy is readily available and environmentally friendly because it does not lead to a net increase in carbon dioxide levels and produces low amounts of sulphur (Akia et al. 2014). A major hindrance to the growth of biomass energy is the competition on food/feed versus fuel. This can be overcome by using non-food biomass sources. Lignocellulosic biomass such as agri-residues, agri-processing byproducts and energy crops which do not compete with food and feed can be used for biofuel production (Munasinghe and Khanal 2010). However, for potential replacement of crude oil by biomass, it is important to note that the petrochemical industry currently consumes three-quarters of the crude oil to cover the demand for liquid hydrocarbon fuels of the

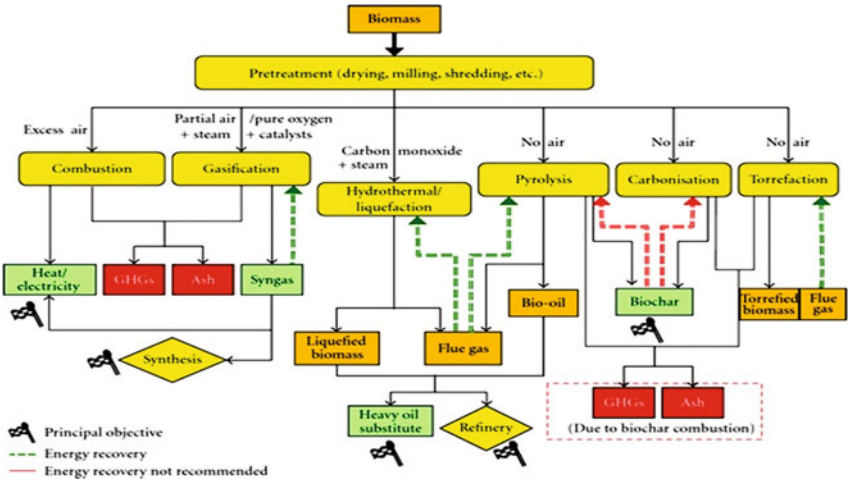

Fig. 1 Biomass thermochemical conversion pathways (Verma et al. 2012)

transportation sector, whereas only a small fraction of the petroleum is utilized in the synthesis of industrial chemicals and other derivatives. Consequently, an effective implementation of biomass in the current energy system will necessarily involve the development of new technologies for the large-scale production of biofuel (Serrano-Ruiz and Dumesic 2011). Presently, 4.7% of liquid transportation fuel production originates from renewable sources (Matthews et al. 2016). The two primary methods for converting biomass to biofuels are thermochemical and biochemical processes. Thermochemical conversion is a major path for producing products such as bioethanol, biodiesel, bio-oil, bio-syngas and biohydrogen. It includes fast pyrolysis, liquefaction, combustion and gasification as seen in Fig. 1. Fast pyrolysis is used for pyrolysis processes with a very short residence time of intense thermal treatment from 0.5–3 s at 400–600 °C. The shorter duration of heat exposure of the biomass in fast pyrolysis process results in increased heat and mass transfer, along with phase transition with chemical reaction kinetics. Long residence times (few minutes to hours) and lower temperature range (200–350 °C) favour charcoal formation (Verma et al. 2012). Liquefaction of biomass to bio-oils involves two main routes, which are hydrothermal and catalytic liquefaction. Hydrothermal liquefaction is based on the superior properties of water at higher temperatures and pressures. The reactivity of biomass is considerable in water, especially under hydrothermal conditions. Water is used as both reactant and solvent in the liquefaction, which prevents any polymerization and prevents the formation of solid products, such as coke and char. Catalytic liquefaction is very similar to hydrothermal liquefaction, however a catalyst is used to reduce the residence time, operating temperature and pressure thereby increasing the quality of liquid products. It was seen that the crude bio-oils produced from catalytic liquefaction flowed easily and were much less viscous than the bio-crude of

noncatalyzed liquefaction (Akia et al. 2014). Gasification typically involves the partial oxidation of biomass into fuel gases at high temperatures (>800 °C). It is usually carried out with air or steam to generate a mixture of CO, H_2, CO_2, and some light hydrocarbons. Gasification processes take place with or without catalysts (Du 2013). Torrefaction is the thermal pretreatment of biomass in an oxygen-free atmosphere over a temperature range of 200–300 °C and has been recognized as an effective method to upgrade biomass into more energy dense and hydrophobic solid fuels. It can be classified into three different severities: light (200–235 °C), mild (235–275 °C) and severe (275–300 °C) torrefaction (Kumar et al. 2017). Combustion of biomass in the presence of air at high temperatures (>800 °C) converts the chemical energy into hot gases. A major drawback is a need for standardized pretreatment processes, such as Sun/drum/vacuum/freeze-drying, grinding, centrifugation and settling, so it is cost intensive. It is employed mostly for biomass with less than 50% of moisture (Kumar et al. 2017).

Biochemical conversion pathway produces liquid or gaseous fuels through fermentation or anaerobic respiration (Akia et al. 2014).The general biochemical conversion pathways consist of five process steps, namely a biomass pretreatment process, a biomass-to-gas conversion process (anaerobic digestion or gasification), a gas cleaning process, a gas-upgrading process, and a the Fischer–Tropsch synthesis (gas-to-liquid process) (Berg 2013). Thermochemical biofuels are getting much more attention lately as these biofuels offer several technical and strategic advantages such as highly developed industrial infrastructure and the biofuels can be produced from virtually all sorts of available biomass in a reasonable timeframe without significant modification in the overall process. In addition, the thermochemical transformation is virtually independent of environmental conditions for production purposes (Verma et al. 2012). At lower reaction temperatures, thermal processing of biomass with catalytic methods offers the possibility of selectively yielding a narrow range of products and reducing the energy requirements of the transformations (Li et al. 2016). Compared with homogeneous catalysts, heterogeneous catalysts can provide clean and recyclable catalyst systems (Guo et al. 2012). The aim of this review is to discuss recent advances in catalysis, specifically nanocatalysts for biofuel production. Metal oxide catalyst (e.g. ZnO), metal supported by metal oxide catalyst (e.g. Au–ZnO), alloy (e.g. AuCu), metal oxide supported by metal oxide (e.g. KF–CaO–Fe_3O_4). Our focus will be on heterogeneous catalysts.

2 Metal Oxide Nanocatalyst for Biofuel Production

A nanocatalyst is a substance or material with catalytic properties that has at least nanoscale dimension, either externally or in terms of internal structures. Nanocatalyst has a large surface-to-volume ratio, and this results in enhanced performance of the catalyst since there is more surface to react with the reactants. Based on the existence of a catalyst in the same phase as the substrate, they can be

classified into two broad groups, heterogeneous catalyst and homogeneous catalyst. Biofuels can be grouped into bioethanol and biodiesel. Bioethanol is the most common biofuel, accounting for more than 90% of total usage. Using sugar and starch biomass as feedstock, it can be produced based on the enzymatic conversion of starchy biomass into sugars, and fermentation of 6-carbon sugars with final distillation of ethanol to fuel grade. While using lingocellulosic materials as feedstock, bioethanol production includes biomass pretreatment to release cellulose and hemicellulose, hydrolysis to release fermentable 5- and 6-carbon sugars, sugar fermentation, separation of solid residues and non-hydrolyzed cellulose and distillation to fuel grade. Biodiesel production is based on transesterification of vegetable oils and fats through the addition of methanol (or other alcohols) and a catalyst, giving glycerol as a co-product. Catalyst plays a major role in the production of biodiesel as it enhances the reaction rate of transesterification process and aids in producing high yields of biodiesel (Hashmi et al. 2016). In recent years, heterogeneous catalysis for biofuel production has been widely studied. Many metal oxides have been examined for the transesterification process of oils and have emerged as potential heterogeneous catalysts; these include alkali earth metal oxides, transition metal oxides, mixed metal oxides, and supported metal oxides (Refaat 2011). The structure of metal oxides is made up of positive metal ions (cations), which consists Lewis acid and negative oxygen ions (anions) which possess Bronsted base as seen in Fig. 2. ZnO is attractive because it is abundant. The use of nanostructures has been proved to improve the catalytic performance of ZnO.

In a thesis, Molina (2013) synthesized ZnO nanorods using a solution approach. The nanorods were used as catalysts to produce biodiesel from olive oil. The nanorods achieved conversions of 94.8% at 150 °C for reaction times of 8 h. They also demonstrated better catalytic performance, which was attributed to their increased degree of crystallinity than conventional ZnO (Molina 2013). Levy et al. (2006) synthesized ZnO nanomaterials in supercritical water (SCW)using a flow-type apparatus and a batch reactor. $ZnAl_2O_4$ was also successfully synthesized with a high specific surface area. Zinc-based oxides were used as catalysts for the conversion of glucose into H_2. For the application of the catalytic reaction by the metal oxide catalysts, biomass conversion in subcritical water was studied to produce H_2. Glucose and H_2O_2 were used as model biomass and oxidant, respectively. Sınağ et al. (2011) studied the effect of ZnO and SnO_2 catalysts on the conversion of cellulose to biofuel as shown in Fig. 3. He presented the contribution of nano ZnO on cellulose conversion at 300 °C and 600 °C and nano SnO_2 was an effective catalyst for cellulose conversion at 400 °C and 500 °C. The lower H_2 production

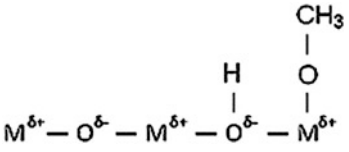

Fig. 2 Surface structure of metal oxides (Zabeti et al. 2009)

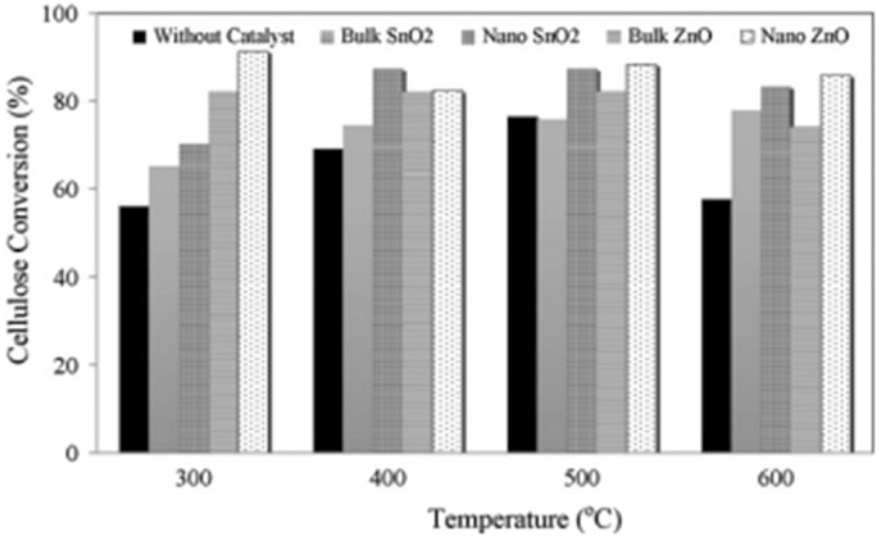

Fig. 3 Effect of nano and bulk ZnO and SnO_2 particles on the conversion degree of cellulose

using the ZnO catalyst synthesized in a flow-type apparatus compared with those in the batch reactor could be explained by the presence of sulphate on the surface of the grain, which is an active poison for the catalyst (Levy et al. 2006).

Wen et al. (2010) prepared a KF–CaO solid base nanocatalyst from KF and CaO with impregnation method and used this to convert Chinese tallow seed oil to biodiesel. The catalyst had a porous structure with the particle size of 30–100 nm. Under the optimal conditions, the biodiesel yield was 96.8% in the presence of as-prepared KF–CaO catalyst (Wen et al. 2010). A promising route for the production of biodiesel via transesterification of soybean oil (SBO) and poultry fat with methanol in quantitative conversions (Fig. 4) at room temperature has been developed (Venkat Reddy et al. 2006) using nanocrystalline calcium oxides as catalysts with high yields. Under the same conditions, laboratory-grade CaO gave only 2% conversion in the case of SBO, and there was no observable reaction with poultry fat (Venkat Reddy et al. 2006).

The catalytic activity for the production of biodiesel with three morphologically different nanocrystalline MgO materials prepared using simple, green and reproducible methods was investigated by Verziu et al. (Verziu et al. 2008) The nanocrystalline samples studied were MgO nanosheets (MgO (I)), conventionally prepared MgO (MgO (II)) and aerogel prepared MgO (MgO (III)). The methods to produce the catalysts include the following:

- 4-methoxy-benzyl alcohol-templated sol-gel process followed by supercritical drying and calcination in air at 773 K (MgO (I)),
- from a commercial MgO that was boiled in water, followed by drying at 393 K, and dehydration under vacuum at 773 K (MgO (II)), and

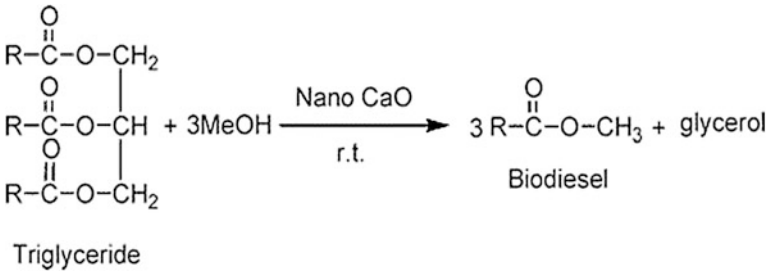

Fig. 4 Synthesis scheme for biodiesel production from soybean oil (Venkat Reddy et al. 2006)

- via hydrolysis of $Mg(OCH_3)_2$ in a methanol–toluene mixture, followed by supercritical solvent removal with the formation of a $Mg(OH)_2$ aerogel that was dehydrated under vacuum at 773 K (MgO (III)).

These catalysts were tested in the transesterification of sunflower and rapeseed vegetable oils at low temperatures, under different experimental conditions; autoclave, microwave and ultrasound. Working with these materials under microwave conditions provided higher conversions and selectivity to methyl esters compared to autoclave or ultrasound conditions. Under ultrasound, a leaching of the magnesium was evidenced as a direct consequence of a saponification reaction. These systems also allowed working with much lower ratios of methanol to vegetable oil than reported in the literature for other heterogeneous systems. Also, these preparations are very green, involving nontoxic reagents and synthesis routes. These metal oxides are active, recyclable heterogeneous catalysts and can be used for transesterification of vegetable oils at low temperatures, as it has been demonstrated for sunflower and rapeseed oils. Thus, these investigations show that nanostructured MgO can be used effectively as a heterogeneous catalyst system for biodiesel transesterification (Verziu et al. 2008). Li et al. (2008) studied the preparation of nano-NiO particles and their applications as catalysts in biomass pyrolysis (an important step in biofuel production). First, nano-NiO particles were prepared via precursors, which were obtained by homogeneous precipitation involving an aqueous solution of nickel nitrate hexahydrate and urea. The formula of the precursor was identified as $NiCO_3{\cdot}2Ni(OH)_2{\cdot}nH_2O$, and it could be completely translated into NiO nanoparticles below 360 °C under an air atmosphere. Furthermore, the catalytic activity of nano-NiO particles in pyrolyzing three biomass components (cellulose, xylan and lignin) was preliminarily investigated, and the results were compared with those of micro-NiO particles under the same conditions. Nano-NiO particles demonstrated a more efficient catalytic effect in biomass pyrolysis over micro-NiO particles. The results indicated that the NiO catalyst could affect the pyrolysis process significantly, with the primary reaction of decomposition to occur at a relatively lower temperature and a marked decrease in the final yield of char as well as the activation energy of biomass pyrolysis (Li et al. 2008).

3 Metal Oxide Supported by Metal Nanocatalyst for Biofuel Production

Calcium oxide (CaO) has been widely used as a solid base nanocatalyst due to its low cost and high activity. Kouzu et al. (2009) found that this high activity was caused by calcium ions leaching into polar phases. These dissolved Ca ions, therefore, act as homogeneous catalysis in the transesterification reaction, leading to an additional cost for post-treatment and a short catalyst lifetime. To improve the catalyst lifetime and stability, metals such as zinc and lanthanum have been used to modify CaO for transesterification reactions. The catalytic activity and catalyst lifetime were dramatically improved by doping with these elements (Yu et al. 1868). Studies by Gurunathan and Ravi (2015) suggested that transesterification reaction could be optimized by using copper-doped zinc oxide (CZO) nanocatalyst for biodiesel production from neem oil as seen in Fig. 5. They synthesized the CZO nanocatalyst by chemical co-precipitation which could be recycled and observed a highly porous and non-uniform surface, which led to the aggregation of CZO nanoparticles in the form of multilayered nanostructures. Biodiesel yield of 97.18% was obtained in 60 min reaction time at 55 C using 10% (w/w) CZO nanocatalyst and 1:10 (v:v) oil: methanol ratio (Gurunathan and Ravi 2015). The heterogeneous solid copper-doped zinc oxide nanocatalyst synthesized by chemical co-precipitation was found to be effective for the production of biodiesel from neem oil. In work done by Baskar et al. (2017) Manganese-doped zinc oxide was used as a heterogeneous catalyst for the production of biodiesel from mahua oil. The synthesized manganese doped zinc oxide nanocatalyst. The SEM and XRD results confirmed the hexagonal structure of the catalyst with the particle size of 24.18 nm. The 8% (w/v) catalyst concentration, 1:7% (v/v) of oil to methanol ratio, 50 min of reaction time and 50 °C of reaction temperature were found to be the optimum

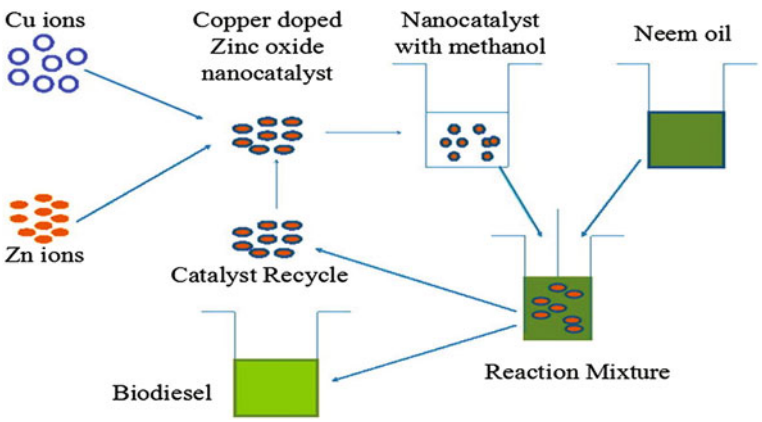

Fig. 5 Biodiesel production from neem oil using copper-doped zinc oxide heterogeneous nanocatalyst (Gurunathan and Ravi 2015)

process condition for the maximum biodiesel yield of 97%. The presence of methyl esters in biodiesel was confirmed by FTIR and GC-MS analysis (Baskar et al. 2017). In the study done by Feyzi et al. (2013), Cs–Al–Fe_3O_4 nanocatalysts were prepared and used for the biodiesel FAME (fatty acids methyl ester) production. This research investigated the effects of different Cs–Al and Cs–Fe molar ratio and calcination conditions on the catalytic performance of Cs–Al–Fe_3O_4 catalysts. Results obtained showed high catalytic activity for biodiesel production and the biodiesel yield reached 94.8% under the optimal conditions (Feyzi et al. 2013). Lithium-impregnated calcium oxide has been prepared by wet impregnation method in nanoparticle form and was examined by Kaur and Ali (2011). Calcium oxide impregnated with 1.75 wt% of lithium was used as a solid catalyst for the transesterification of *karanja* and *jatropha* oil, containing 3.4 and 8.3 wt% of free fatty acids, respectively. The complete transesterification of *karanja* and *jatropha* oils was achieved in 1 and 2 h, respectively, at 65 °C, utilizing 12:1 molar ratio of methanol to oil and five wt% (catalyst/oil, w/w) of catalyst (Kaur and Ali 2011). Iron–tin (ISnO) oxide nanoparticles were used as catalysts for the transesterification of soybean oil as well as esterification of soybean oil fatty acids in the study done by Alves et al. (2014). High yields, ca. 84%, were achieved, after 1 h reaction time at 200 °C. The oxide was magnetically recovered and reused four times without loss of its activity. ISnO also demonstrated catalytic activity for *macauba* oil, a highly acidic substrate. Mixed iron–cadmium (ICdO) and iron–tin (ISnO) oxides were prepared and tested as catalysts in biodiesel production through hydrolysis, esterification and transesterification reactions using soybean oil. The surface area of the ICdO catalyst was twice that of ISnO. Despite this difference in a surface area, no significant catalytic activity difference was observed in the esterification reaction (Alves et al. 2014).

In the study done by Montero et al. (2010), caesium incorporation via co-precipitation on nanocrystalline MgO under supercritical conditions generates $Cs_2Mg(CO_3)_2$nanocrystallites. Wet impregnation proved less effective for modifying MgO nanocrystals. A strong synergy between Cs and Mg components in the co-precipitated material dramatically enhanced the rate of tributyrin transesterification with methanol about undoped MgO and homogeneous Cs_2CO_3 catalysts. Caesium was an effective promoter of MgO solid base catalysts for the transesterification of tributyrin with methanol. Doping via co-precipitation under solvothermal regimes promoted the formation of $Cs_2Mg(CO_3)_2$ nanocrystallites with significantly enhanced base site densities and polarizabilities compared with undoped MgO nanocrystals (Montero et al. 2010).

4 Alloy

Cu–Co bimetallic nanoparticles coated with carbon layers have been developed through direct heating treatment of bimetallic oxide precursors incipiently deposited with polyethene glycol (Chen et al. 2017). The simultaneous formation of carbon

layers over the nanoparticles protects them from oxidation and deactivation. The nanocatalyst performed excellently in the chemoselective hydrogenolysis of 5-hydroxymethylfurfural (HMF) to 2, 5- dimethylfuran (DMF). DMF is a biofuel that can be produced through selective hydro-de-oxygenation of a platform molecule from cellulose (5-hydromethylfurfural, HMF).The yield of DMF reached approximately 99.4% and exceeded the results of supported noble metal catalysts. The catalyst showed good recyclability and recoverability in a six-run recycling test. This work provides a novel and insightful strategy to develop low-cost and high-performance hydrotreating catalysts based on base metals for industrial organic process and valorization of renewable biomass (Chen et al. 2017). Hybrid nanocatalysts containing enzymes and metallic nanoparticles have also been used for biodiesel production. In work done by Xie and Ma et al. (2010), lipase was covalently immobilized onto magnetic Fe_3O_4 nanoparticles by using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDAC) as an activating agent, and the bound lipase was used to catalyze the transesterification of vegetable oils with methanol to produce fatty acid methyl esters. It was determined that the immobilized lipase exhibited better resistance to temperature and pH inactivation in comparison to free lipase. The conversion of soybean oil to methyl esters reached over 90% in the three-step transesterification when 40% immobilized lipase was used. Moreover, the lipase catalyst could be used for three times without a significant decrease in the activity (Xie and Ma 2010). Bimetallic gold–silver core–shell nanoparticles (Au–Ag) were synthesized at room temperature, where gold nanoparticles served as seeds for continuous deposition of silver atoms on its surface. The catalytic activity of these nanoparticles towards biodiesel production from sunflower oil through transesterification was studied by Banerjee et al. (2014), and a yield of 86.9% biodiesel was attained. The fuel properties of the synthesized biofuel were at par with standard biofuel. Further, the catalyst showed sustained activity for three cycles of transesterification (Banerjee et al. 2014). Deng et al. (2011) synthesized hydrotalcite-derived particles with Mg/Al molar ratio of 3/1 by a co-precipitation method using urea as precipitating agent, subsequently with (MHT) microwave-hydrothermal treatment, and followed by calcination at 773 K for 6 h. These particles were micro-sized mixed Mg–Al oxides as characterized by SEM and AFM. But actually, they were nanosized according to the calculations from XRD data. Because of their strong basicity, the nanoparticles were further used as a catalyst for biodiesel production from *jatropha* oil after pretreatment. At the optimized condition, biodiesel yield of 95.2% was achieved. The catalyst can be reused for eight times. The catalyst was only 7.3 nm by calculation, but according to AMF analysis, they congregated to form a layered structure with size as large as 0.941 mm width and 381 nm thickness. The main reasons for catalyst deactivation were the surface absorption of by-product glycerol as well as the collapse of the layered structure. After removing the glycerol on the surface, the catalyst was reused for eight times (Deng et al. 2011).

5 Metal Oxide Supported by Metal Oxide Nanocatalyst for Biofuel Production

Biodiesel is mainly composed of ethyl esters and fatty acid methyl esters (FAEE and FAME) and is taken to be one of the clean and environmentally friendly sources of energy. Biodiesel is produced from fats and oils via esterification and transesterification in the presence of homogeneous or heterogeneous acid–base catalysts (Basumatary 2013). Heterogeneous catalysts are preferred because they are much easier to separate, have lower production cost and display environmentally friendly features when compared with homogeneous catalysts (Borges and Díaz 2012). Traditional heterogeneous catalysts (for example, zeolites, single-metal oxides, hydrotalcite and supported alkali metal/metal ion) have been widely demonstrated to have high efficiency for biodiesel production. However, there are some drawbacks with these catalysts; they show weak strength, expensive and complex to prepare, have relatively small surface area, low catalytic performance, have little resistance to atmospheric CO_2 and water pollution, require high temperature and pressure and alcohol–oil ratios (Chang et al. 2014). These are the reasons why biodiesel is not produced in large scale when these traditional catalysts are employed. To remove the drawbacks mentioned above, the deployment of solid mixed metal oxide catalysts as heterogeneous catalysts have stimulated substantial interest recently for the production of biodiesel. Solid mixed metal oxide catalysts typically refer to those comprising of two or more metal oxides in their makeup. For example, base mixed metal oxide catalysts and acid-based bifunctional mixed metal oxide catalysts.

- **Base mixed metal oxide catalysts for biodiesel production**

Base mixed metal oxide catalysts are typically doped with MgO or CaO to boost their catalytic performance. These types of catalysts are very active for the transesterification reaction in the production of biodiesel. In these catalytic processes, the used raw materials (fats or oils), with a certain amount of free fatty acid content are considered to be necessary; otherwise, it will cause base catalyst poisoning and affect the quality of the biodiesel. Some research works carried out on mixed metal oxide catalysts are detailed in Tables 1 and 2.

CaO- and MgO-based mixed metal oxide catalysts have stimulated interest in research community due largely to their exceptional catalytic performance. However, these catalysts usually show poor recyclability and poor resistance to water and acid (Chang et al. 2014). Thus, these forms of catalysts are mostly used in the transesterification of oil-bearing low acid and water contents. On the other hand, acid mixed metal oxide catalysts prepared from corresponding transition metal salts could simultaneously catalyze the esterification and transesterification reactions though harsh reaction conditions are required such as high temperatures, high alcohol/oil ratios, and longer reaction times (Chang et al. 2014).

Table 1 CaO-based mixed metal oxide catalysts

S/N	Catalyst	Oil	Catalyst amount (wt %)	Alcohol/oil ratio	Reaction temp (°C)	Reaction time	FAME (%)	Ref
1	CaO–NiO	*Waste cottonseed oil*	5	15:1	65	4 h	>99	Kaur and Ali (2014)
2	CaO–CeO_2	*Refined palm oil (acid value< 0.4 $mg_{KOH}g^{-1}$)*	5	20:1	85	3 h	95	Thitsartarn and Kawi (2011)
3	CaO–ZrO_2 (molar ration: Ca–Zr = 0.5)	*Waste cooking oil*	10	30:1	65	2 h	92.10	Dehkordi and Ghasemi (2012)
4	CaO–Al_2O_3	*Palm oil*	6	12:1	65	5 h	98.64	Zabeti et al. (2010)
5	CaO–La_2O_3	*Jatropha curcas oil 13.60 $mg_{KOH}g^{-1}$*	4	24:1	65	6 h	86.51	Teo et al. (2014)
6	CaO–MgO(Mg/Ca = 0.5)	*Jatropha curcas oil*	3	25:1	120	3 h	90	Taufiq-Yap et al. (2011)
7	CaO–ZnO	*Sunflower oil*	3	12:1	60	45 min	>90	Rubio-Caballero et al. (2009)
8	CaO–La_2O_3	*Well-refined soybean oil*	5	20:1	58	1 h	94.30%	Yan et al. (2009)
9	CaO–ZnO	*Sunflower oil*	2	10:1	60	4 h	97.50	Kesić et al. (2012)
10	CaO(16 wt%)–ZnO	*Sunflower oil*	1.3	12:1	60	2 h	>90	Alba-Rubio et al. (2010)
11	KF–CaO–Fe_3O_4	*Stillingia oil*	4	12:1	65	3 h	>95	HusY (2011)

Table 2 MgO-based mixed metal oxide catalysts

S/N	Catalyst	Oil	Catalyst amount (wt%)	Alcohol/oil ratio	Reaction temp (°C)	Reaction time	FAME (%)	Ref
1	MgO–ZnO	*Jatropha curcas oil*	3	25:1	120	3 h	83	Lee et al. (2013)
2	TiO_2–MgO	*Waste cooking oil*	5	30:1	150	6 h	>85	Wen et al. (2010)
3	LaMgO	*Cottonseed oil*	5	54:1	65	20 min	96.00	Mutreja et al. (2014)
4	MgAlCe	*Soybean oil*	5	9:1	67	3 h	>90	Dias et al. (2012)
5	20-Sr–MgO	*Refined palm oil*	3	6:1	60	75 min	96	Faungnawakij et al. (2012)

- **Acid Mixed Metal Oxide catalysts for Biodiesel Production**

In order to address the high free fatty acid content in raw oils used for biodiesel production, different acid mixed metal oxide catalysts have been developed. Table 3 shows some of the works carried on the production of biodiesel using acid mixed metal oxide catalysts.

6 Synthesis and Characterization of Nanoparticles for Biofuel Production

- **Green synthesis of nanoparticles**

Metal nanoparticles have been studied extensively due to their exceptional electrical, optical and catalytic properties (Coe et al. 2002; Bruchez et al. 2013). For the optimization and utilization of nanosized particles' physical or chemical properties, great research efforts have been focused on how to control their shapes and sizes which are needed in the modification of their optical and physicochemical properties (Bar et al. 2009). For the synthesis of metal nanoparticles, different techniques have been explored which are mainly divided into physical and chemical means. The methods include electrochemical reduction (Liu and Lin 2004), heat evaporation (Smetana et al. 2005), chemical reduction (Yu 2007), photochemical reduction (Mallick et al. 2005), etc. Mostly, to prevent nanoparticles from aggregation, surface passivator reagents are employed (Bar et al. 2009). However, a large number of surface passivators (mostly organic) such as mercapto acetate, thiourea, thiophenol, etc., are toxic to the environment when a large number of nanoparticles are produced (Bar et al. 2009). In order to address this drawback, green biosynthesis of nanoparticles is gaining traction in nanoparticles research community due to the need to produce environmentally friendly alternatives. For example, research efforts have been put into the production of biosynthetic inorganic materials (e.g. metal nanoparticles) synthesized from microorganisms (Shahverdi et al. 2007; Basavaraja et al. 2008).

Rao and Pennathur (2017) discussed the green and environmentally friendly method of synthesis of cadmium sulphide (CdS) nanoparticles from the aqueous cell-free extract of *Chlamydomonasreinhardtii*. From morphological analysis by electron microscopy, the authors (Rao and Pennathur 2017) observed the presence of spherical particles measuring roughly 5 nm under HRTEM. From structural analysis using X-ray diffraction and FTIR, the authors (Rao and Pennathur 2017) confirmed the cubic CdS nanoparticles that were capped with algal proteins. Optical analyses of the nanostructures showed an increase in the band gap to 2.93 eV. Photoluminescence spectrum of CdS nanoparticles revealed emission peaks at 430 nm and 470 nm. The nanoparticles were found to be stable in solution with a zeta potential of −30.7 mV. The authors (Rao and Pennathur 2017) thus concluded that the one-step strategy employed with algal cell-free extract to produce CdS

Table 3 Production of biodiesel with acid mixed metal oxide catalysts

S/N	Catalyst	Oil	Catalyst amount (wt%)	Alcohol/ oil ratio	Reaction temp (°C)	Reaction time (h)	FAME (%)	Ref
1	SO_4^{2-}–ZrO_2–TiO_2	Oleic acid	5	16:100	65	6	Esterification: 42.2 transesterification: 88	Shao et al. (2013)
2	Fe_2O_3–SiO_2	Crude Jatropha oil	15	218:1	220	3	Transesterification >99	Suzuta et al. (2012)
3	SnO_2–SiO_2	Soybean oil	5	24:1	180	5	Transesterification: 81.7 esterification: 94.6	Xie et al. (2011)
4	WO_3–SnO_2	Soybean oil	5	30:1	110	5	Transesterification: 79.2	Xie and Wang (2013)
5	SO_4^{2-}–TiO_2–SiO_2	Waste soybean oil	10	20:1	120	3	Transesterification: 88	Shao et al. (2013)

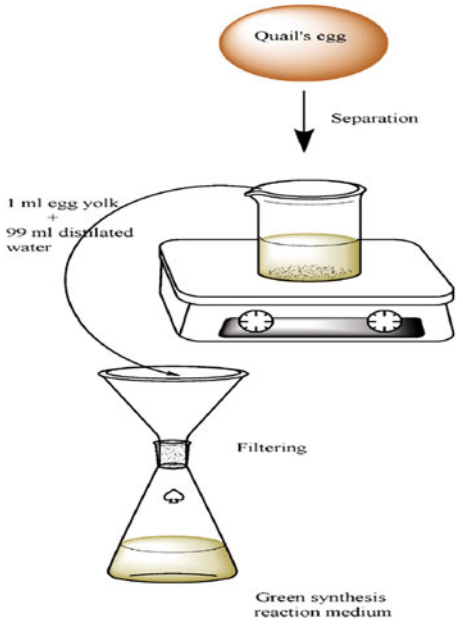

Fig. 6 The processing for the green reaction medium (Nadaroglu et al. 2017)

nanoparticles is an environmentally friendly and feasible economical approach for the large-scale synthesis of CdS nanoparticles for deployment in photocatalysis.

Nadaroglu et al. (2017) used quail egg yolk (shown in Fig. 6) for the synthesis of platinum nanoparticles of 7–50 nm. The authors (Nadaroglu et al. 2017) employed the high protein and vitamin contents of the yolk for green synthesis in the reaction medium without addition of any chemical reducing agent. Reaction conditions and parameters (pH, temperature, time and concentration) were controlled in order to attain the optimal reaction conditions to obtain platinum nanoparticles. The results obtained showed that the maximum platinum nanoparticles were synthesized at 20 °C, pH 6.0 for 4 h. Also, the optimal concentration of metal ions was established as 0.5 mM. For the characterization of the platinum nanoparticles, the authors (Nadaroglu et al. 2017) employed UV–Vis spectroscopy, XRD and SEM (shown in Fig. 7). The analysis showed that the synthesis of platinum nanoparticles was performed based on direction, morphology and quantity characterization. Synthesized platinum nanoparticles have a wide range of applications catalysis, electrocatalysis, nanotechnology, pharmaceutical and chemical processes.

Bar et al. (2009) effectively synthesized silver nanoparticles from $AgNO_3$ using an environmentally friendly green resource latex of *Jatropha curcas* as capping as well as reducing agent. For the characterization of the synthesized nanoparticles, the authors (Bar et al. 2009) used X-ray diffraction, HRTEM and UV–Vis absorption spectroscopy. X-ray diffraction analysis showed that the nanoparticles were of the face-centred cubic structure. A comparison of the radius of nanoparticles obtained from HRTEM image with the optimized cavity radius of the cyclic peptides present

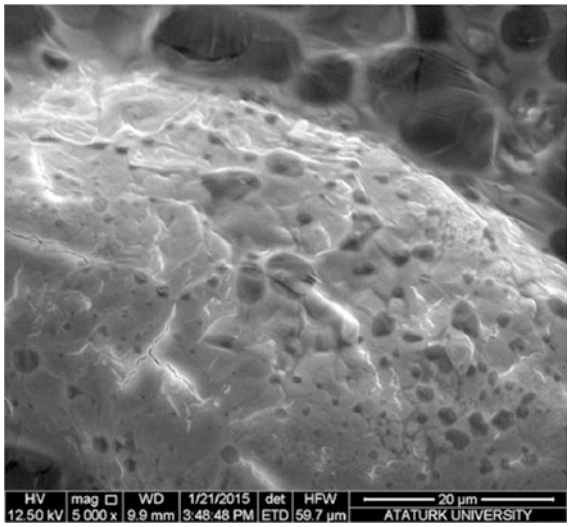

Fig. 7 SEM micrographs of synthesized platinum nanoparticles (Nadaroglu et al. 2017)

within the latex revealed that the particles having radius 10–20 nm are mostly stabilized by the cyclic peptides. Also, HRTEM and UV–Vis spectroscopy showed that there are two major distributions of particles size; the smaller particles are majorly stabilized by the cyclic octapeptide (curacy cline A) and cyclic nonapeptide (curacy Cline B). However, the larger and irregular shaped particles are majorly stabilized by the curcain, the enzyme found in the latex. The authors (Bar et al. 2009) thus recommended further experiment for size-selective synthesis of silver and gold nanoparticles using cyclic peptide found in the latex.

In the field of nanotechnology, synthesis of metal nanoparticles via eco-friendly route is gaining momentum (Sharmila et al. 2017). Sharmila et al. (2017) presented an environmentally friendly biogenic synthesis of palladium nanoparticles (PdNPs) using leaf extract of *Filiciumdecipiens*. For characterization, the synthesized PdNPs were studied by TEM, UV–Vis spectroscopy, FTIR and XRD. The PdNPs formation was established by UV–Vis spectrophotometer and spherical-shaped PdNPs with a size range of 2–22 nm was detected in TEM analysis. Energy dispersive X-ray spectroscopy (EDS) analysis established the presence of palladium in the synthesized nanoparticles. XRD pattern confirmed the crystalline nature of PdNPs. The phytochemicals and proteins were identified by their functional groups in FTIR spectrum and revealed the amide and amine groups present in *Filiciumdecipiens* which could have been involved in the bio-reduction reaction for PdNPs synthesis (Sharmila et al. 2017).

Wang et al. (2016) prepared $S_2O_8^{2-}$–ZrO_2 (solid superacid catalyst), by one-pot method (a new synthesis route), treated with $(NH_4)_2S_2O_8$ (ammonium persulfate) through vapour phase hydrolysis to increase biodiesel production with expired soybean oil as a reactant. For the synthesized catalyst characterization, the authors (Wang et al. 2016) used TEM, XRD and NH3-temperature programmed desorption

(NH3-TPD) to determine the optimal pretreatment conditions and to understand the role of the active sites for transesterification. At 500 °C, $S_2O_8^{2-}$–ZrO_2 calcined was seen to compose of tetragonal phase ZrO_2 microcrystallites TEM examination and showed an amorphous phase by XRD characterization. The microcrystallites which anchored more $S_2O_8^{2-}$ had abundant super acid and displayed high catalytic activity in the transesterification under mild reaction conditions. The reaction parameters over the catalyst were optimized and both the conversion of soybean oil and selectivity of biofuel reached 100% under the conditions of 4 h of reaction time, 110 °C of reaction temperature and 20:1 of methanol-to-oil molar ratio. The author (Wang et al. 2016) observed the catalyst to show high stability in the reactions and during cyclic utilization, no sulphur leaching was found in the biodiesel products.

- **Non-green synthesis of nanoparticles**

Banerjee et al. (2014) synthesized bimetallic gold-silver core–shell nanoparticles (Au@Ag NPs) at room temperature, in which pre-synthesized gold nanoparticles (AuNPs) served as seeds for continuous deposition of silver atoms on its surface. For the characterization, the core–shell structure of the nanoparticles was analyzed by TEM (shown in Fig. 8), UV–Vis spectroscopy and energy dispersive X-ray (EDX). The authors (Banerjee et al. 2014) further studied the catalytic activity of the nanoparticles towards biodiesel production from sunflower oil through transesterification. The confirmation for biofuel synthesis was performed with FTIR spectroscopy. The fuel properties were determined by standard ASTM (American Society for Testing and Materials) protocols. The authors (Banerjee et al. 2014) observed that at a certain temperature, reaction time and catalyst concentration, 86.9% (highest yield) of biodiesel was achieved. On further analysis, it was discovered that the properties of the synthesized biofuel are the same with conventional biofuel. Furthermore, the catalyst sustained its activity for three cycles of transesterification processes.

Chen et al. (2017) synthesized Cu–Co bimetallic nanoparticles coated with carbon layers through direct heating of bimetallic oxide precursors. Polyethene glycol over the precursors acts as the reductant for metal species and carbon sources of carbon layers. The as-synthesized nanocatalyst performed well in chemoselective hydrogenolysis of 5-hydroxymethylfurfural to 2, 5-dimethylfuran yielding up to 99.4% of dimethylfuran, which surpassed the results obtained when supported noble metals catalysts were used. The Co-based catalysts exhibit higher performance than Cu-based catalysts. For the characterization, the synthesized bimetallic nanocatalysts were characterized in details by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The results obtained showed that the bimetallic nanoparticles were encased in carbon shells, capable of protecting them deactivation and oxidation. The authors (Chen et al. 2017) carried out the six-run test, and the synthesized catalyst showed excellent recoverability and recyclability. The authors (Chen et al. 2017) thus concluded that the method employed provides an insightful and novel approach to

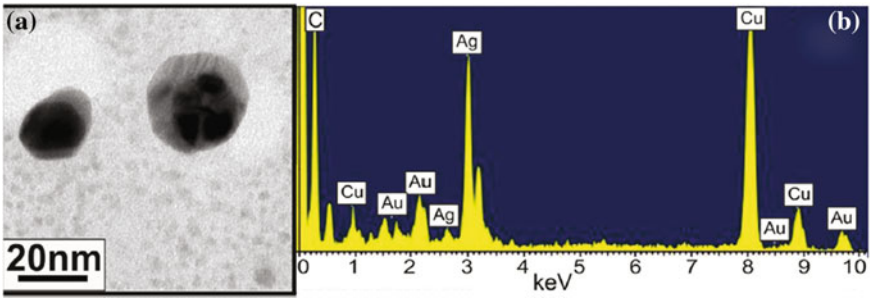

Fig. 8 Typical TEM image (**a**) and EDX spectrum (**b**) confirming the presence of both gold and silver in the Au–Ag core–shell bimetallic NPs Banerjee et al. (2014)

developing high-performance and low-cost hydrotreating catalysts based on base metals for deployment in renewable biomass.

Lapin et al. (2016) synthesized cerium oxide nanoparticles in water, ethanol and ethanol-water solution for the first time by the use of laser (fundamental harmonic of nanosecond Nd: YAG) ablation of bulk metallic cerium target. The authors (Lapin et al. 2016) obtained nanocrystalline powders of cerium oxide from the dispersion of average crystallite size of 17–19 nm. For the characterization, Raman spectroscopy and XRD were used for the phase composition of the nanoparticles. Carbon impurity (0.3–0.5% by weight) was discovered to be present on the surface of CeO2 particles which would probably have appeared during the drying of the dispersion. The authors (Lapin et al. 2016) thus recommended that further studies of nanocrystalline ceria should be carried out by laser ablation in the liquid phase that would include the study of surface properties and composition, as well as the study of their functional characteristics for subsequent use catalytic applications (Fig. 9).

Table 4 gives a summary of some of the articles reviewed on nanocatalysts for biofuel production; it shows the oil used, the catalyst size, the synthesis method and the conversion obtained.

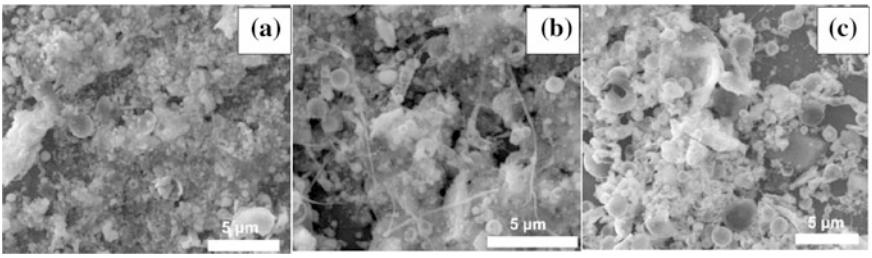

Fig. 9 Morphology of CeO_2nanopowders (the SEM image): from water (**a**), water-ethanol (**b**) and ethanol dispersion (**c**) (Lapin et al. 2016)

Table 4 Nanocatalysts used for biofuel production with their sizes and methods of synthesis

S/N	Oil	Catalyst size (nm)	Synthesis method	Conversion (%)	Recyclability (cycles)	Catalyst type	REF
1	*Olive oil*		Solution approach	94.80		ZnO	Molina (2013)
2	*Chinese tallow seed oil*	30–100	Impregnation method	96.80		KF–CaO	Wen et al. (2010)
3	*Soybean oil*	20	Purchased	99	4	CaO	Venkat Reddy et al. (2006)
4	*Sunflower oil*	50–200	Sol-gel	99	5	MgO	Verziu et al. (2008)
5	*Neem oil*	40.62	Chemical co-precipitation	97.10	6	Cu–ZnO	Gurunathan and Ravi (2015)
6	*Mahua oil*	24.18	Co-precipitation	97	5	Mn–ZnO	Baskar et al. (2017)
7	*Sunflower oil*	30–35	Precipitation	94.80	4	Cs–Al–Fe_3O_4	Feyzi et al. (2013)
8	*Karanja and jatropha oil*	50–70	Wet impregnation	99	0	Li–CaO	Kaur and Ali (2011)
9	*Soybean oil*	34.8	Co-precipitation	84	4	Fe–SnO	Alves et al. (2014)
10	*5-hydromethylfurfural*	Oct-60	Direct heating treatment	99.40	6	Cu–Co	Chen et al. (2017)
11	*Soybean oil*	11.2	Co-precipitation	90	3	Fe_3O_4	Xie and Ma (2010)
12	*Sunflower oil*	28	Deposition	86.90	3	Au–Ag	Banerjee et al. (2014)
13	*Jatropha oil*	7.3	Co-precipitation	95.20	8	Mg–Al	Deng et al. (2011)

7 Conclusion

This work has reviewed the literature on nanocatalysts for biofuel production. The review carried out focused on heterogeneous catalysts such as metal oxide (e.g. ZnO), metal supported by metal oxide (e.g. Au–ZnO), alloy (e.g. Cu–Co), metal oxide supported by metal oxide (e.g. KF–CaO–Fe_3O_4); their synthesis and characterization (with much emphasis on green production). This is to highlight what has been done and the stage reached, in order to give researchers a clear idea of an expected contribution to knowledge in nanocatalysts for biofuel production.

References

Akia M, Yazdani F, Motaee E, Han D, Arandiyan H (2014) A review on conversion of biomass to biofuel by nanocatalysts. Biofuel Res J 1:16–25

Alba-Rubio AC, Santamaría-González J, Mérida-Robles JM, Moreno-Tost R, Martín-Alonso D, Jiménez-López A et al (2010) Heterogeneous transesterification processes by using CaO supported on zinc oxide as basic catalysts. Catal Today 149:281–287

Alves MB, Medeiros F, Sousa M, Rubim J, Suarez P (2014) Cadmium and tin magnetic nanocatalysts useful for biodiesel production. J Braz Chem Soc 25:2304–2313

Banerjee M, Dey B, Talukdar J, Chandra Kalita M (2014) Production of biodiesel from sunflower oil using highly catalytic bimetallic gold–silver core–shell nanoparticle. Energy 69:695–699

Banerjee M, Dey B, Talukdar J, Kalita MC (2014b) Production of biodiesel from sunflower oil using highly catalytic bimetallic gold–silver core–shell nanoparticle. Energy 69:695–699

Bar H, Bhui DK, Sahoo GP, Sarkar P, De SP, Misra A (2009) Green synthesis of silver nanoparticles using latex of Jatropha curcas. Colloids Surf A 339:134–139

Basavaraja S, Balaji S, Lagashetty A, Rajasab A, Venkataraman A (2008) Extracellular biosynthesis of silver nanoparticles using the fungus Fusarium semitectum. Mater Res Bull 43:1164–1170

Baskar G, Gurugulladevi A, Nishanthini T, Aiswarya R, Tamilarasan K (2017) Optimization and kinetics of biodiesel production from Mahua oil using manganese doped zinc oxide nanocatalyst. Renew Energy 103:641–646

Basumatary S (2013) Transesterification with heterogeneous catalyst in production of biodiesel: a review. J Chem Pharm Res 5:1–7

Berg HO (2013) Comparison of conversion pathways for lignocellulosic biomass to biofuel in Mid-Norway. In: Løvås T, Lånke AF, Kempegowda RS, F. F. I. O. T. I. F. E.-O. P (eds). Norges Teknisk-Naturvitenskapelige Universitet, Institutt for energi- og prosessteknikk

Borges M, Díaz L (2012) Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: a review. Renew Sustain Energy Rev 16:2839–2849

Bruchez M, Moronne M, Gin P, Weiss S, Alivisatos AP (1998) Semiconductor nanocrystals as fluorescent biological labels. Science 281:2013–2016

Chang F, Zhou Q, Pan H, Liu XF, Zhang H, Xue W et al (2014) Solid mixed-metal-oxide catalysts for biodiesel production: a review. Energy Technol 2:865–873

Chen B, Li F, Huang Z, Yuan G (2017) Carbon-coated Cu-Co bimetallic nanoparticles as selective and recyclable catalysts for production of biofuel 2, 5-dimethylfuran. Appl Catal B Environ 200:192–199

Chen B, Li F, Huang Z, Yuan G (2017b) Carbon-coated Cu-Co bimetallic nanoparticles as selective and recyclable catalysts for production of biofuel 2, 5-dimethylfuran. Appl Catal B 200:192–199

Coe S, Woo W-K, Bawendi M, Bulović V (2002) Electroluminescence from single monolayers of nanocrystals in molecular organic devices. Nature 420:800–803

Dehkordi AM, Ghasemi M (2012) Transesterification of waste cooking oil to biodiesel using Ca and Zr mixed oxides as heterogeneous base catalysts. Fuel Process Technol 97:45–51

Deng X, Fang Z, Liu Y-H, Yu C-L (2011) Production of biodiesel from Jatropha oil catalyzed by nanosized solid basic catalyst. Energy 36:777–784

Dias APS, Bernardo J, Felizardo P, Correia MJN (2012) Biodiesel production over thermal activated cerium modified Mg-Al hydrotalcites. Energy 41:344–353

Du Z (2013) Thermochemical conversion of microalgae for biofuel production. In: Ruan R, Hu B, Morrison R, Tschirner U (eds). ProQuest Dissertations Publishing

Faungnawakij K, Yoosuk B, Namuangruk S, Krasae P, Viriya-empikul N, Puttasawat B (2012) Sr–Mg mixed oxides as biodiesel production catalysts. ChemCatChem 4:209–216

Feyzi M, Hassankhani A, Rafiee HR (2013) Preparation and characterization of Cs/Al/Fe_3O_4 nanocatalysts for biodiesel production. Energy Convers Manag 71:62–68

Guo P, Huang F, Zheng M, Li W, Huang Q (2012) Magnetic solid base catalysts for the production of biodiesel. J Am Oil Chem Soc 89:925–933

Gurunathan B, Ravi A (2015) Process optimization and kinetics of biodiesel production from neem oil using copper doped zinc oxide heterogeneous nanocatalyst. Bioresour Technol 190:424–428

Hashmi S, Gohar S, Mahmood T, Nawaz U, Farooqi H (2016) Biodiesel production by using CaO-Al2O3 Nano catalyst. IJERS

HusY GY (2011) Nano–magneticcatalystKF/CaO–Fe_3O_4 for biodiesel production. Appl Energy 88:2685

Kaur M, Ali A (2011) Lithium ion impregnated calcium oxide as nano catalyst for the biodiesel production from karanja and Jatropha oils. Renew Energy 36:2866–2871

Kaur M, Ali A (2014) Potassium fluoride impregnated CaO/NiO: an efficient heterogeneous catalyst for transesterification of waste cottonseed oil. Eur J Lipid Sci Technol 116:80–88

Kesić Ž, Lukić I, Brkić D, Rogan J, Zdujić M, Liu H et al (2012) Mechanochemical preparation and characterization of CaO·ZnO used as catalyst for biodiesel synthesis. Appl Catal A 427:58–65

Kouzu M, Yamanaka S-Y, Hidaka J-S, Tsunomori M (2009) Heterogeneous catalysis of calcium oxide used for transesterification of soybean oil with refluxing methanol. Appl Catal A Gen 355:94–99 (28 Feb 2009)

Kumar G, Shobana S, Chen W-H, Bach Q-V, Kim S-H, Atabani AE et al (2017) A review of thermochemical conversion of microalgal biomass for biofuels: chemistry and processes. Green Chem 19:44–67

Lapin I, Shabalina A, Svetlichnyi V (2016) Synthesis and characterization of CeO2 nanoparticles. Key Eng Mater 281–287

Lee HV, Taufiq-Yap Y, Hussein MZ, Yunus R (2013) Transesterification of Jatropha oil with methanol over Mg–Zn mixed metal oxide catalysts. Energy 49:12–18

Levy C, Watanabe M, Aizawa Y, Inomata H, Sue K (2006) Synthesis of nanophased metal oxides in supercritical water: catalysts for biomass conversion. Int J Appl Ceram Technol 3:337–344

Li J, Yan R, Xiao B, Liang DT, Lee DH (2008) Preparation of nano-NiO particles and evaluation of their catalytic activity in pyrolyzing biomass components. Energy Fuels 22:16–23 (01 Jan 2008)

Li H, Fang Z, Smith Jr RL, Yang S (2016) Efficient valorization of biomass to biofuels with bifunctional solid catalytic materials. Progress Energy Combust Sci 55:98–194

Liu Y-C, Lin L-H (2004) New pathway for the synthesis of ultrafine silver nanoparticles from bulk silver substrates in aqueous solutions by sonoelectrochemical methods. Electrochem Commun 6:1163–1168

Mallick K, Witcomb MJ, Scurrell MS (2005) Self-assembly of silver nanoparticles in a polymer solvent: formation of a nanochain through nanoscale soldering. Mater Chem Phys 90:221–224
Matthews LR, Niziolek AM, Onel O, Pinnaduwage N, Floudas CA (2016) Biomass to liquid transportation fuels via biological and thermochemical conversion: process synthesis and global optimization strategies. Ind Eng Chem Res 55:3203–3225 (30 Mar 2016)
Molina C (2013) ZnO nanorods as catalyts for biodiesel production from olive oil. In: Carreon M, Sumanasekera G, Willing G (eds). ProQuest Dissertations Publishing
Montero JM, Wilson K, Lee AF (2010) Top Catal 53:737. https://doi.org/10.1007/s11244-010-9461-4
Munasinghe PC, Khanal SK (2010) Biomass-derived syngas fermentation into biofuels: opportunities and challenges. Bioresour Technol 101:5013–5022
Mutreja V, Singh S, Ali A (2014) Potassium impregnated nanocrystalline mixed oxides of La and Mg as heterogeneous catalysts for transesterification. Renew Energy 62:226–233
Nadaroglu H, Gungor AA, Ince S, Babagil A (2017) Green synthesis and characterisation of platinum nanoparticles using quail egg yolk. Spectrochim Acta Part A Mol Biomol Spectrosc 172:43–47
Rao MD, Pennathur G (2017) Green synthesis and characterization of cadmium sulphide nanoparticles from Chlamydomonas reinhardtii and their application as photocatalysts. Mater Res Bull 85:64–73
Refaat A (2011) Biodiesel production using solid metal oxide catalysts. Int J Environ Sci Technol 8:203–221
Rubio-Caballero JM, Santamaría-González J, Mérida-Robles J, Moreno-Tost R, Jiménez-López A, Maireles-Torres P (2009) Calcium zincate as precursor of active catalysts for biodiesel production under mild conditions. Appl Catal B 91:339–346
Serrano-Ruiz JC, Dumesic JA (2011) Catalytic routes for the conversion of biomass into liquid hydrocarbon transportation fuels. Energy Environ Sci 4:83–99
Shahverdi AR, Minaeian S, Shahverdi HR, Jamalifar H, Nohi A-A (2007) Rapid synthesis of silver nanoparticles using culture supernatants of Enterobacteria: a novel biological approach. Process Biochem 42:919–923
Shao GN, Sheikh R, Hilonga A, Lee JE, Park Y-H, Kim HT (2013) Biodiesel production by sulfated mesoporous titania–silica catalysts synthesized by the sol–gel process from less expensive precursors. Chem Eng J 215:600–607
Sharmila G, Fathima MF, Haries S, Geetha S, Kumar NM, Muthukumaran C (2017) Green synthesis, characterization and antibacterial efficacy of palladium nanoparticles synthesized using Filicium decipiens leaf extract. J Mol Struct 1138:35–40
Smetana AB, Klabunde KJ, Sorensen CM (2005) Synthesis of spherical silver nanoparticles by digestive ripening, stabilization with various agents, and their 3-D and 2-D superlattice formation. J Colloid Interface Sci 284:521–526
Sınağ A et al (2011) Catalytic hydrothermal conversion of cellulose over SnO_2 and ZnO nanoparticle catalysts. J Supercrit Fluids 56(2):179–185
Suzuta T, Toba M, Abe Y, Yoshimura Y (2012) Iron oxide catalysts supported on porous silica for the production of biodiesel from crude Jatropha oil. J Am Oil Chem Soc 89:1981–1989
Taufiq-Yap Y, Lee HV, Yunus R, Juan JC (2011) Transesterification of non-edible Jatropha curcas oil to biodiesel using binary Ca–Mg mixed oxide catalyst: effect of stoichiometric composition. Chem Eng J 178:342–347
Teo SH, Rashid U, Taufiq-Yap YH (2014) Biodiesel production from crude Jatropha Curcas oil using calcium based mixed oxide catalysts. Fuel 136:244–252
Thitsartarn W, Kawi S (2011) An active and stable CaO–CeO 2 catalyst for transesterification of oil to biodiesel. Green Chem 13:3423–3430
Venkat Reddy CR, Oshel R, Verkade JG (2006) Room-temperature conversion of soybean oil and poultry fat to biodiesel catalyzed by nanocrystalline calcium oxides. Energy Fuels 20:1310–1314 (01 May 2006)

Verma M, Godbout S, Brar SK, Solomatnikova O, Lemay SP, Larouche JP (2012) Biofuels production from biomass by thermochemical conversion technologies. Int J Chem Eng 2012 (542426):1–18. https://doi.org/10.1155/2012/542426

Verziu M, Cojocaru B, Hu J, Richards R, Ciuculescu C, Filip P et al (2008) Sunflower and rapeseed oil transesterification to biodiesel over different nanocrystalline MgO catalysts. Green Chem 10:373–381

Wang H-G, Shi G-L, Yu F, Li R-F (2016) Mild synthesis of biofuel over a microcrystalline S 2 O 8 2 −/ZrO_2 catalyst. Fuel Process Technol 145:9–13

Wen L, Wang Y, Lu D, Hu S, Han H (2010) Preparation of KF/CaO nanocatalyst and its application in biodiesel production from Chinese tallow seed oil. Fuel 89:2267–2271

Wen Z, Yu X, Tu S-T, Yan J, Dahlquist E (2010b) Biodiesel production from waste cooking oil catalyzed by TiO_2–MgO mixed oxides. Biores Technol 101:9570–9576

Xie W, Ma N (2010) Enzymatic transesterification of soybean oil by using immobilized lipase on magnetic nano-particles. Biomass Bioenergy 34:890–896

Xie W, Wang T (2013) Biodiesel production from soybean oil transesterification using tin oxide-supported WO 3 catalysts. Fuel Process Technol 109:150–155

Xie W, Wang H, Li H (2011) Silica-supported tin oxides as heterogeneous acid catalysts for transesterification of soybean oil with methanol. Ind Eng Chem Res 51:225–231

Yan S, Kim M, Salley SO, Ng KS (2009) Oil transesterification over calcium oxides modified with lanthanum. Appl Catal A 360:163–170

Yu D-G (2007) Formation of colloidal silver nanoparticles stabilized by Na + –poly (γ-glutamic acid)–silver nitrate complex via chemical reduction process. Colloids Surf B 59:171–178

Yu X, Wen Z, Li H, Tu S-T, Yan J (2011) Transesterification of Pistacia chinensis oil for biodiesel catalyzed by CaO–CeO2 mixed oxides. Fuel 90:1868–1874

Zabeti M, Wan Daud WMA, Aroua MK (2009) Activity of solid catalysts for biodiesel production: a review. Fuel Process. Technol. 90:770–777

Zabeti M, Daud WMAW, Aroua MK (2010) Biodiesel production using alumina-supported calcium oxide: an optimization study. Fuel Process Technol 91:243–248