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ZrO_2-based catalysts for biodiesel production: A review

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ABSTRACT

ZrO_2-based catalysts are remarkable catalyst with unique advantageous in transesterification and esterification for biodiesel production. Various modifications have been conducted refer to a specified surface properties consist of surface acidity/basicity, specific surface area and porosity, hydrophobicity, and catalysts stability. Summary on the basic concept on catalyst synthesis, applicability for various feedstocks along with their reusability aspect in biodiesel production are discussed in this review. Even though the activity of the catalyst is depending on many factors including the oil feedstocks, reaction temperature, molar ratio of oil to methanol, and other conditions, the controllable surface properties of catalyst is a benefit of ZrO_2-based catalysts. The recyclability and reusability of the catalyst become important aspect for developing a sustainable biodiesel production in the perspective of green chemistry. In addition, future perspective to make sure the applicability of the catalyst for a sustainable process by life cycle assessment is highlighted in this review.

1. Introduction

Growing demand for fossil fuels have been a global attention and forced the exploration of renewable energy. Accordingly, the potency of biomass especially oil-producing plants and some animal fats are considered as the energy resource due to its sustainability. Biodiesel is a well-known alternative energy resource derived from vegetable oils, and animal fat via transesterification reaction [1–3]. It is comprised of mono-alkyl esters of long-chained fatty acids and pure biodiesel is designated B100. The transesterification is notified as simple process that has been widely adopted. It is reflected by 93% more energy than energy invested in production, higher compared to ethanol production which showed yields of 25%. The ratio between invented energy and produced energy was calculated based on all steps in whole process including machinery, facility and laborer energy use, transportation, fossil fuel use, fertilizer and pesticide [4]. The ratio could reach more value depending on the source of oil, for example the ratio of 2.7 is obtained from the use of rapeseed oil [5]. From the green production perspective, biodiesel is known as the greener fuel as the greenhouse gas is 41% lower compared to fossil fuel [3]. These advantages of biodiesel over ethanol come from lower agricultural inputs and more efficient conversion of feedstocks to fuel [4,6]. The blending of biodiesel into diesel fuel reduces emissions of CO, PM10, VOC, and SOx during combustion, and better relative to diesel and bioethanol. Those benefits forced the development of biodiesel as major alternative to fossil [4,7].

The simple process of biodiesel conversion of oil into biodiesel or fatty acid methyl esters (FAMEs) is a simple process, and has been well-known to be applicable in industrial scale. Transesterification itself is the chemical process to convert triglycerides in oil into Fatty Acid Methyl Esters (FAME or biodiesel) and glycerol as byproduct. The reaction occurs faster in presence catalyst, either homogeneous catalyst (usually NaOH or KOH) or heterogeneous catalyst, at moderate temperature of about 60–80 °C and atmospheric pressure. For the fast conversion, usually alcohol utilized could be methanol (methanolysis) or ethanol (ethanolysis). However, generally the methanolysis occurs faster compared to ethanolysis, and in addition, higher ethanol to oil ratio is required to get a similar yield to the methanolysis [Fig. 1].

The general reaction equation of the conversion provides an abundantly sources of triglyceride for biodiesel production, which in general, are divided into plant oil and animal oil. Not only common plant oils such as palm, castor, jatropha, rapeseed, etc., the use of waste source such as animal fat and fisheries industrial waste have been assed as the potential feedstock. However, in general, the applicability for industrial scaling is closely related with the cost of the process. Some factors such

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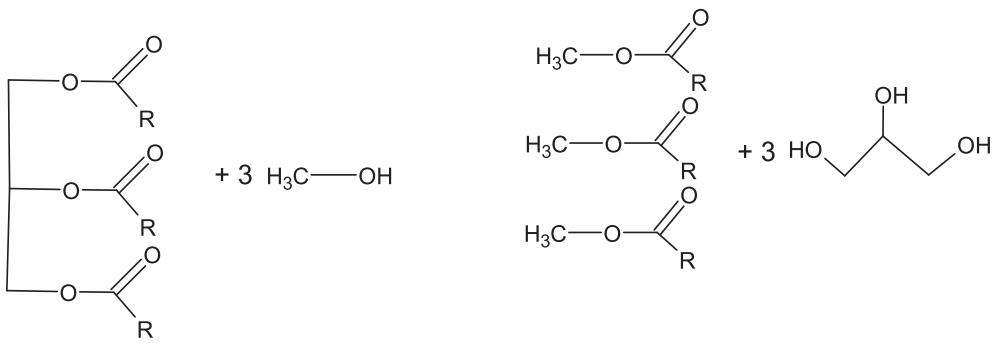

Fig. 1. General equation of transesterification by methanol (methanolysis).

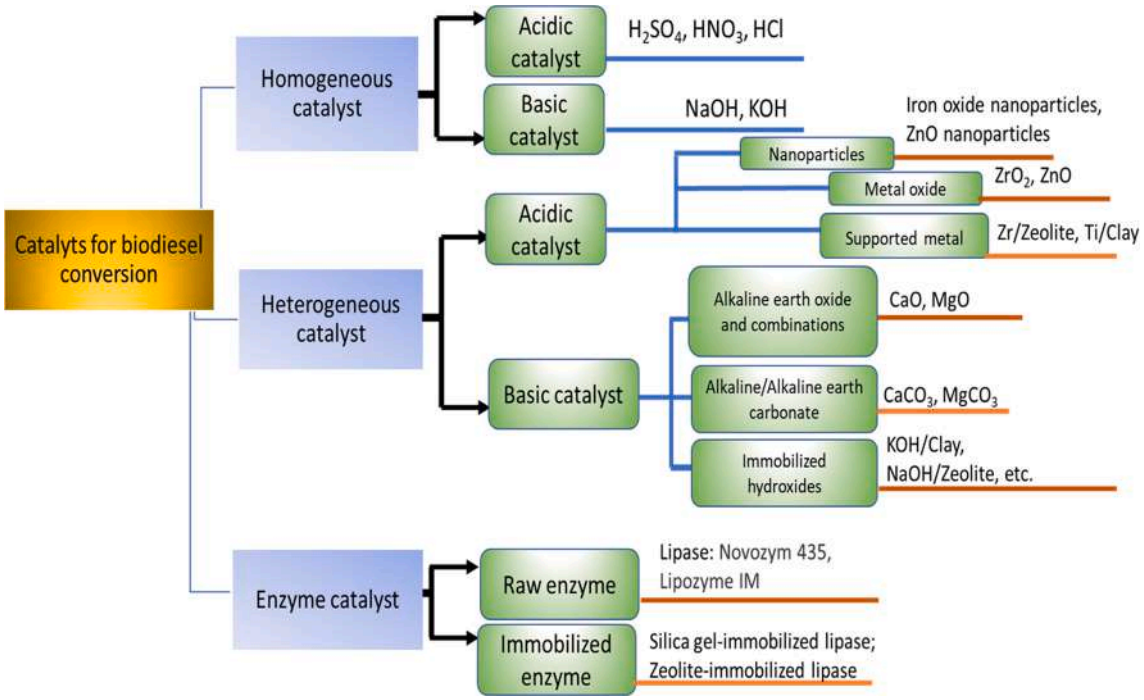

Fig. 2. Type of catalysts for biodiesel production [9].

as the feedstock supply, infrastructure, and the energy consumed for the production are the dynamic and essential variables to production economics. Within the process, minimizing and optimizing catalysts are also important in the chemical processing. The easy in separation and reusability are the main factors to be considered for heterogeneous catalyst use beside of homogeneous catalyst. Heterogeneous catalysts should be highly efficient, chemically stable, and recyclable with maintained activity [8].

Fig. 2 presents types of catalyst for biodiesel production from various oil sources. It can be seen that in general, the catalysts are classified into heterogeneous, homogeneous and enzyme catalysts. Homogenous catalytic system gives advantageous related with high reaction yields (over 97%) at a moderate temperature (25–70 °C) and relatively short reaction period (to 2 h). As many other organic reactions, reaction variables such as methanol to oil molar ratio, catalyst dosage, temperature and time influence the yield. However, the drawbacks of homogeneous catalyst usage is correlated with the difficulties in catalyst separation and consumable catalyst [10]. For example, in the use of NaOH for the production, it will be diluted in the reaction system and cannot be recoverable. Moreover, the rest of the catalyst requires to be neutralized or removed with a large amount of hot water, leads to a large amount of industrial wastewater. The high volume of water will influence the corrosivity of the reaction system which directly influences the cost of infrastructure [8,11,12]. From the use of enzyme as catalyst, although some benefits such as high purity, easy separation with glycerol, and possibility to use ethanol as safer alcohol rather than methanol, it has some limitations. The enzymatic process expresses a long time required method, requires a strict optimum pH and temperature, and expensive in cost that are the reasons for this inappropriateness for being applied in large scale industries. In order to provide reusability and the easiness in separation, immobilizations of enzymatic into a support or nanoparticles are now in progress. However, from many research works, it is conclusively obtained that the yields are still less than that of those homogeneous or heterogenous catalysts [13–16].

Consideration based on the ease of catalyst separation, the environmental and economic benefits and also technical feasibility of biodiesel production suggest the heterogeneous acid-catalyzed esterification and transesterification for biodiesel production. As the alcoholysis/methanolysis in the reaction system is in liquid phase, heterogeneous catalysts are the solids; that are divided into acidic and basic inorganic solid. Some oxides such as CaO and MgO that are well-known materials in this type. The less interaction caused by the immiscible catalyst that become a trigger of the solid catalyst due to the less soluble alkali earth oxides [6]. Without any additional efforts such as stirring, it

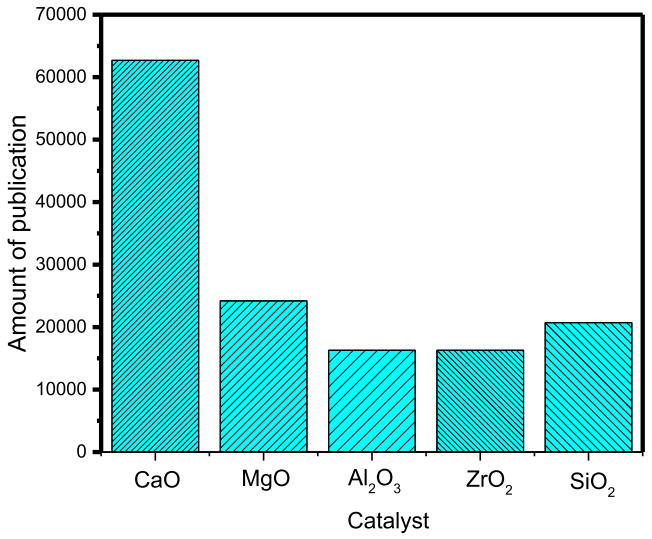

Fig. 3. Popularity of ZrO_2-based catalyst for biodiesel production (Source: Google Scholar, accessed: April 14th 2022).

affects to the less interaction between the oil, alcohol and the catalyst.

Beside of those metal oxides, zirconium dioxide (zirconia, ZrO_2) is a remarkable heterogeneous catalyst and catalyst support for transesterification reaction. ZrO_2 is characterized to have modifiable acid-base surface properties, good stability and corrosion resistance, even in the harsh reaction conditions. In addition, catalyst support, ZrO_2 exhibits better stability than the traditional catalyst supports such as silica, alumina and carbonate minerals. Even though many esterification reactions were reported to be effective over ZrO_2, but for biodiesel production, ZrO_2 was usually in combination with other active metals or metal oxides. For example, several studies on canola oil and soybean oil over ZrO_2 was not effective and give no yield, but it gave extremely high activity by the combination with alkali metals and sulphate ions [17,18]. Many other many modifications to ZrO_2 in order to enhanced the effectiveness of catalysis in biodiesel production, which mainly monitored by the catalytic conversion and reusability. In many cases, the tunable surface properties of ZrO_2 in transesterification catalysis including controllable surface acidity-basicity is a tricky and has been explored interestingly. Conclusively, various modifications govern the reaction productivity. The popularity of ZrO_2-based catalyst for biodiesel production and the comparison with other metal oxide presented in Fig. 3.

As can be seen from Fig. 3, CaO is superior catalyst to other metal oxide for biodiesel production. The high trend in the utilization of CaO as catalyst is related with abundant source and possibility to use biogenic CaO from many waste-derived materials[19–23]. In addition, compared to MgO, CaO has greater basicity to assure the faster transesterification occurred. Some animal wastes such as crustacean shell, egg shell, chicken, pig and cow are the examples for this biogenic CaO, which recognized as cost-effective catalyst and potential to be developed in a cycle of green economy of producing biodiesel [24,25]. Even though the use of CaO from animal bones exhibited a good consistency in the performance for the transesterification mechanism, longer time of reaction and higher catalyst loading in industrial practices was reported [26]. Hence, the use of biogenic CaO become non-economically feasible and impractical, in terms of operating cost [25]. In addition, the rapid loss of activity and catalyst leaching also become the other problems related with the reusability. In addition, based on basic catalysis conducted by CaO and MgO, they could not be effective for water- or high free fatty acid- containing feedstock cause of the side reaction of saponification become the cumbersome system. The combination of CaO with other metal oxide such as MgO and also modifications using alkali or alkali earth and dopping were attempted to cover these problems. Such combinations of CaO with various scheme for enhancement have been proven to be successfully increase the reusability and yield, but then, it affects the increasing production cost [27]. Refer to many challenges in biodiesel production, mainly in the strategy of catalysis process, ZrO_2-based catalysts becomes interesting materials. Therefore, this work is to review the use of ZrO_2-based catalysts in biodiesel production. The contents of this paper can be described from following aspects: (1) the recent development progresses in heterogeneous catalytic conversion of biodiesel; (2) the development of ZrO_2-based catalysts; (3) the main factors influencing catalytic activity of ZrO_2-based catalysts; (4) the future perspective in the utilization of ZrO_2-based catalysts. The purpose of this work is to highlight the further research areas of ZrO_2-based catalysts, and discuss the possibly to be applied in

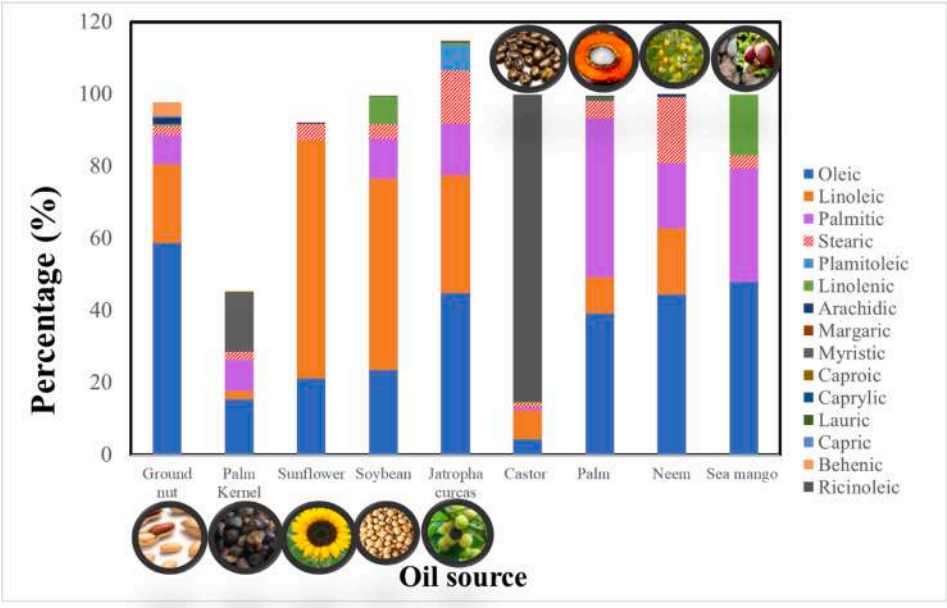

Fig. 4. Oil feedstocks of biodiesel and their compositions.

Table 1
ASTM D6751 and EN 14214 standards for biodiesel fuels and ASTM D 975 for biodiesel [30].

Specification	Unit	EN 14214:2003	ASTM D 6751-07b	Specification	Unit	EN 14214:2003	ASTM D 6751-07b
Density 15 °C	g/cm^3	0.86–0.90	0.88	Acid value	mgKOH /g	0.5 max	0.5 max
Viscosity 40 °C	mm^2/s	3.5–5.0	1.9–6.0	Methanol	%mass	0.20 max	0.2 max or Fp < 130 °C
Distillation	% @ °C		90%,360 °C	Ester content	%mass	96.5 min	
Flashpoint (Fp)	°C	120 min	93 min	Monoglyceride	%mass	0.8 max	
CFPP	°C	* country specific		Diglyceride	%mass	0.2 max	
Cloud point	°C		* report	Triglyceride	%mass	0.2 max	
Sulphur	mg/kg	10 max	15 max	Free glycerol	%mass	0.02 max	0.02 max
CCR 100%	%mass		0.05 max	Total glycerol	%mass	0.25 max	0.24 max
Carbon residue (10 %dist. residue)	%mass	0.3 max		Iodine value		120 max	
Sulphated ash	%mass	0.02 max	0.02 max	Linolenic acid ME	%mass	12 max	
Oxid ash	%mass			C(x:4) & greater unsaturated esters	%mass	1 max	
Water	mg/kg	500 max	500 max	Phosphorus	mg/kg	10 max	10 max
Total contamination	mg/kg	24 max		Alkalinity	mg/kg		
Cu corrosion max	3 h/50 °C	1	3	Gp I metals (Na,K)	mg/kg	5 max	5 max
Oxidation stability	hrs;110 °C	6 h min	3 h min	GpII metals (Ca,Mg)	mg/kg	5 max	5 max
Cetane number		51 min	47 min				

greener and sustainable biodiesel production.

2. Recent development progresses in heterogeneous catalytic conversion of biodiesel

This necessitates of biodiesel production bring the development of low-cost production and selection of catalyst. As mentioned in the background part, various reasons are the consideration of choosing heterogeneous catalyst instead of homogeneous catalyst. Even though other recent method and technology such as enzymatic process and supercritical fluids, but they are valued as non-economic procedure and still requires to reduce costs and increase yield. In addition, the challenge is that the different feedstocks for biodiesel production have a great influence on the type of catalysts used. The process occurs by reacting vegetable oil with alcohol in the presence of a catalyst. Various catalysts have been utilized with acidic and basic catalysts being the most common. However, the applications of supercritical fluids or enzymes are also being explored in order to reduce costs and increase yield. Beside of its role as the crucial factor as the barrier for the cost of production, different oil feedstock will also determine the preferable acid or basic catalyst utilized for the optimum production. Such oil with high free fatty acid (FFA) got effectivity in acid catalysis to minimize the side reaction of saponification, and vice versa.

From these descriptions, the challenges of catalysis in biodiesel are high-efficient, low-cost and regenerable catalyst that appropriate to the feedstock as the different oil contains different component of triglyceride [28,29]. Fig. 4 shows some of dominant feedstock in biodiesel production with their compositions.

Recent studies have also reported the increased use of heterogeneous catalysts for the production of biodiesel from low-cost starting materials. The different feedstocks for biodiesel production have a great influence on the type of catalysts used. Refined vegetable oils have been extensively used as the primary feedstocks for the transesterification process. However, waste oils from cooking oils and animal fat can also be utilized because of their availability and low cost [28]. Other low-cost oils from non-edible plant sources are also suitable for the production of biodiesels. These methods aid in the recycling of the waste oil and the prevention of food and fuel competition for energy production. Despite their potential, the waste oils and animal fat are however seen as low-quality feedstocks compared to refined vegetable oils because of their FFA content. For biodiesel production to be effective for low-quality feedstocks, some form of pretreatment is required. Animal fats usually contain bone and meat particles as well as organic matter. These must be filtered using a cellulose filter and other pretreatment steps include water removal, steam distillation, and bleaching [3]. These low-quality feedstocks may be inexpensive but their high FFAs make them unsuitable for the conventional direct base catalyzed transesterification process due to soap formation. In addition, the produced biodiesel has to meet with the ASTM D6751 and EN 14214 standards as listed in Table 1.

The high yield, reusable and long lifetime features are the character of catalyst designed for production feasibility. Notably, the solid catalyst with high specific surface area and surface activity were preferred, and regarding to these properties, modified porous solids and nano catalyst were developed and got tremendous attentions [31].

Based on heterogeneous catalysis theory, surface interaction among reactants and catalyst surface is the basic mechanism of solid-catalyzed

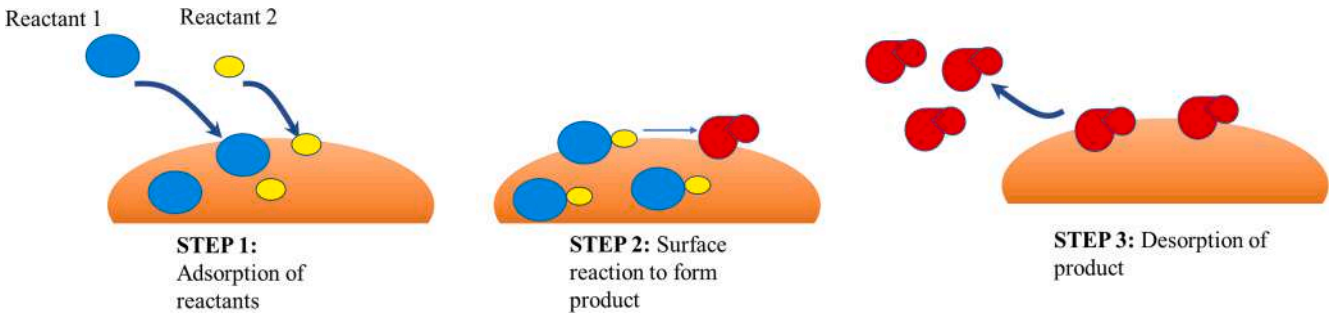

Fig. 5. General mechanism of heterogeneous catalysis.

reaction. It requires the capability of catalyst to adsorb or intensively interact with the reactant molecules, in this case, oil and methanol for transesterification. Fig. 5 represents general mechanism of the heterogeneous catalysis.

Modifications to zeolite, silica and clay minerals were reported with enhanced yield in biodiesel conversion from various feedstocks. The increased converted soybean oil of more than 80% yield by ethylic transesterification was achieved over CuO, ZnO and CeO_2 supported on bentonite [32,33], and a yield of 97% was derived from waste cooking oil as over by CaO-modified clay [34,35] are the examples of the importance of clay-based catalysts. All of the metal oxide-modified clay gave higher yields compared to acid-treated clay, which refer to the role of specific surface area more dominant compared to the surface acidity for soybean oil conversion. Similar trend was exhibited by the increased yield of the use of ZnO/SiO_2 compared to SiO_2 for rice bran oil conversion, but there was conclusively obtained that the increasing conversion was linearly correlated with increased specific surface area, total surface acidity and ratio of Lewis to Bronsted acidity [36,37]. The presence of higher surface area leads to the shorter time and lower temperature of reaction to achieve optimum yield. It reflected by the use of SrO_2/SiO_2 for soybean oil conversion at 65 °C and 30 min of reaction for more than 96% yield [38].

Conclusively, the effectivity of the reaction mechanism is attributed to the combination of surface area, pore size distribution, quantitative surface acidity/basicity, and are also determined by the character of modifier; metal or metal oxide. Catalysts of Pd, Ru, and Ag supported on natural zeolite are the representatives for this explanation [39]. Increasing catalyst performance is the function of surface area, pore size distribution and surface acidity, that are the impact of metal loading content.

The initial evaluation of the prepared catalyst is mainly specific surface area and surface acidity/basicity. Such gas sorption analyses consist of BET specific surface area, pore distribution and pore volume are usually measured based on N_2 adsorption/desorption profile. This surface analysis is usefully predicting the pore structure of modified nanocomposites, in term of comparison on pore distributions. For surface acidity/basicity measurement, several techniques can be adopted i.e. acid/base-back titration method, pyridine adsorption followed by Fourier-Transform Infra-Red analysis, and NH_3-Temperature Program Desorption (NH_3-TPD), and CO_2-TPD [40]. In the back titration method for basicity determination, as the solid mixed with acid solution in larger amount, the basic surface sites will adsorb the acid and represented as the surface basicity, and vice versa for surface acidity measurement [12,41]. Such n-butylamine solution and other alkylamine were usually used as probe solution for acidity, and acetic acid or citric acid for surface basicity. In more detail, determination of acidity/basicity with profiling the strength of acidity/basicity can be determined by Hammet titration method [42]. In addition, for determination of Lewis and Broensted acidity, pyridine adsorption followed by FTIR analysis can be conducted [43].

The internal factor of the characteristics of support such as Si/Al ratio of zeolite also govern these parameters [39]. The surface acidity, surface character, and pore size distribution provided by zeolite support is depending on Si/Al, and it is directly correlated with the hydrophobicity or hydrophilicity of the surface. As an example, zeolite beta provided favorable adsorption of oleic acid molecules than the adsorption of the polar ethanol molecules, resulting in higher coverage of oleic acid molecules on the surface of zeolites and higher conversion rate of esterification [39].

The more efficient interaction with reactants to conduct effective surface reaction with high yield of biodiesel was demonstrated by the use of nanosized metal oxides such as ZnO, SrO_2, and CaO [44–46]. The reusable catalyst until 5th cycles with the yield of more than 99% was expressed by nano-ZnO, and becomes interesting aspect of longer life time of catalyst for sustainable biodiesel production from soy bean oil [44]. The effectivity of nanoparticles is assigned by the more efficient surface binding efficiency within surface mechanism that contributes to the decreasing activation energy of the reaction [46,47].

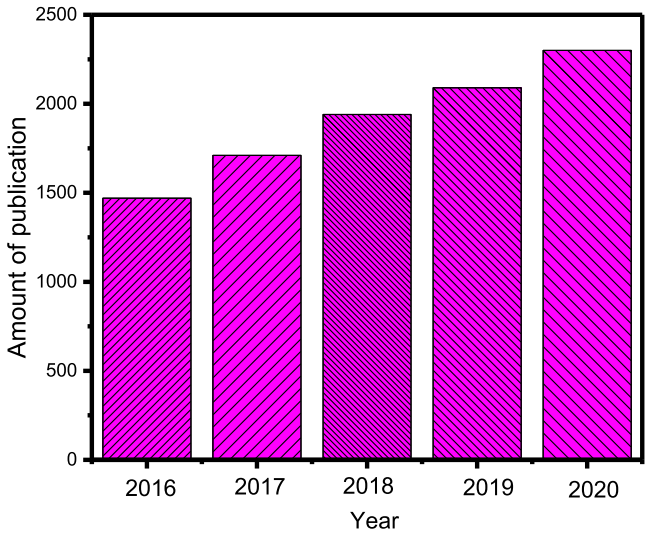

Fig. 6. Trend on the publications of ZrO2-based catalysis in biodiesel production (Source: Google scholar, accessed April 14th 2022).

3. ZrO_2-based catalyst in biodiesel production

On the basis of those important aspects, zirconia-based catalysts were developed to cover the technical problems in industrial scale, and moreover evaluated the green-economic value of the process. With the synthesizing and designing material from pure precursor, catalyst performance can be optimized easily. Some factors such as the influencing impurities in the catalysts that take effects on catalytic activity may be faced by the use of natural-derived minerals like natural zeolites or natural clays. It sometimes reduces the energy efficiency of the process in whole production. These considerations are reflected by the increasing attention on ZrO_2-based catalysts for biodiesel during 2018–2021, as reflected by chart in Fig. 6.

In material technology, ZrO_2 is well-known ceramic material which is widely applied for fuel cell, sensor, catalysts, photocatalysis, and catalyst supports. As catalyst and catalyst support, ZrO_2 brings the unique physical properties attributed to both acid and base active centers on the surface. Capability of surface to attract and adsorb organic molecules is the main factor for its role as heterogeneous catalyst. In addition, thermal stability and tunable porosity make it superior for some high-temperature organic reactions, for examples alkylation and oxidation reactions [48,49]. As an example, pure ZrO_2 is a stable with high activity in oxidation-reduction catalysis [49]. The capability of ZrO_2 surface to oxidize is according to the formation of OH functional groups formed by dissociative activated hydrogen react to form water. As many other heterogeneous catalysts, the tailoring the surface properties and porosity is a strategy for optimize the catalytic activity. By this, the strategy is laid on the synthesis and preparation method.

Precipitation method is the simplest technique of ZrO_2 synthesis. Usually, the precipitate of $Zr(OH)_4$ was derived by reacting Zr precursors such as of zirconium acetate, zirconium chloride, and zirconium oxide chloride in an alkali condition (pH 10) [50–55]. Calcination is the next process to convert $Zr(OH)_4$ to ZrO_2 is by calcination that also determine kind of phase formed [56,57]. There are three phases of ZrO_2 that possibly to form, namely cubic (*c*-ZrO_2), monoclinic (*m*-ZrO_2) and tetragonal (*t*-ZrO_2) with the crystal structure presented in Fig. 7.

The phase formation is depending on the precipitation conditions, pH of the medium, and temperature of crystallization. However, all three phases can be obtained via the amorphous condition (*a*-ZrO_2) from the precipitation or other step of the oxide formation [58]. *c*-ZrO_2 and *t*-

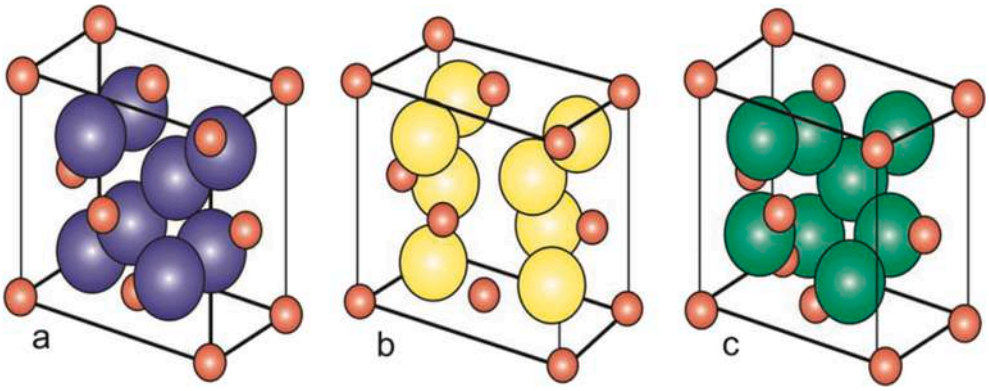

Fig. 7. Crystal structure of (a) *m*-ZrO_2, (b) *t*-ZrO_2, and (c) *c*-ZrO_2 [Copyright permission from InTech Open].

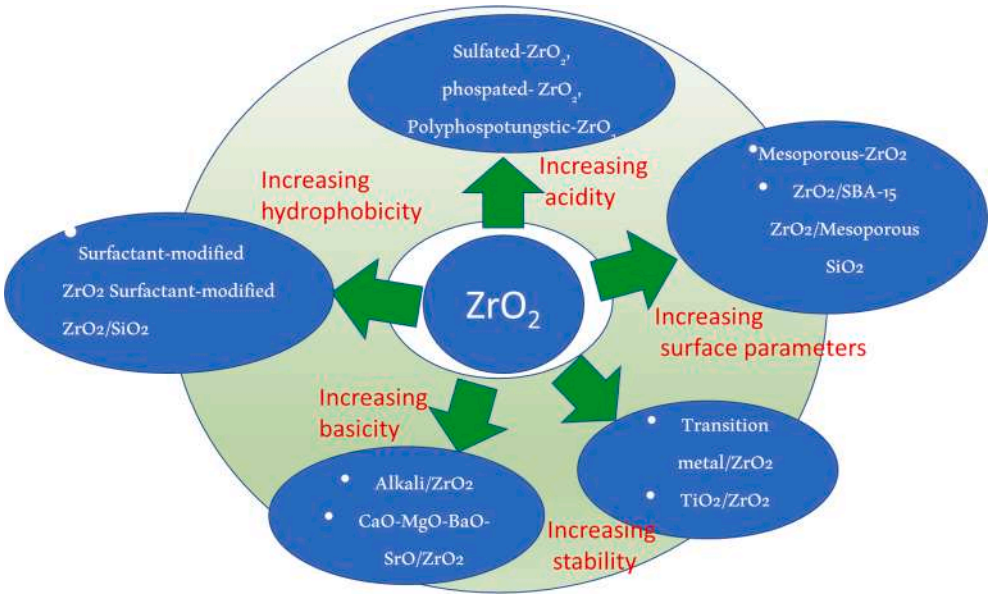

Fig. 8. Various modifications on ZrO_2-based catalysts for biodiesel production.

ZrO_2 are the metastable phases which strongly depending on the temperature of the crystallization. Schematically, the transitions can be ascribed as following equation [59]:

$$a - ZrO_2 \rightarrow m - ZrO_2 \,(\ 400^{\circ}C) \rightarrow t - ZrO_2\,(700^{\circ}C)$$

Based on DTA-TGA analysis, the formation of *t*-ZrO_2 was achieved at 390–400 °C and at the increasing temperature to 700 °C the phase transitioned into *m*-ZrO_2 [57]. By using alkyl-zirconium and organic template in the sol-gel synthesis method, the mesoporous ZrO_2 is usually obtained. The precursors such as zirconium t-butoxide and zirconium t-isopropoxide are the examples for sol-gel mechanism, which the creation of mesoporous structure is usually designed by the presence of surfactants as template. A high specific surface area of mesoporous zirconia with the value of 270 $m^2.g^{-1}$ has been reported by utilize zirconium t-butoxide in sol-gel method, higher than that of obtained by the precipitation method with value at around 60–80 $m^2.g^{-1}$ [57,60]. Other various methods such as hydrothermal, sol-gel, and solvothermal method also their intensified procedure for creating higher porosity and surface area by addition of ultrasound and microwave-irradiations were attempted [61–63]. However, the increasing porosity is not always in linear with the increasing catalytic activity, as many other factors are in combinative and depending on the reaction type. In more detail for example, the activity of ZrO_2 in syngas conversion from aromatic compounds is governed by the phase of ZrO_2 by directing C–O Activation and C–C Coupling. Temperature programmed desorption study indicated that the capability of *m*-ZrO_2 to adsorb CO is higher than *t*-ZrO_2, which can easier facilitate the C–O activation [64]. In more specific reaction such as photocatalysis, different phase and composition directly influences the band gap energy that is main parameter for the effectivity of reaction.

In biodiesel catalysis, ZrO_2 is mainly act as catalyst support with specified enhanced feature. Fig. 8 presents the main scheme of ZrO_2 modification which mainly divided into modification for enhancing basicity, acidity, specific surface area, and hydrophobicity. Table 2 presents the list of various ZrO_2-based catalyst for biodiesel production from many kinds of oil feedstock.

From Table 2, it is seen that modified zirconia composites have been examined widely for various seed oil with optimized conditions. It is understood that different component of the plant oil is a crucial factor determining the yield, and conclusively represents the suitable catalyst.

The use of sulphated zirconia is the most popular ZrO_2-based catalyst in biodiesel production. The preparation of material is also simpler as the zirconia obtained by either precipitation or sol-gel method, furthermore impregnated with sulfuric acid is the source of sulfate. Other method for the synthesis is the mixing of $Zr(OH)_4$ with sulfuric acid followed by calcination [68]. The specific surface area of sulfated zirconia is the concentration of sulfuric acid, pH of precipitation and calcination temperature, which indirectly correlated with the presence

Table 2
Some catalyzed biodiesel conversions using ZrO_2-based catalysts.

Catalyst	Oil feedstock	Remark	Maximum Yield (%)/Time of reaction	Reference
SO_4^{2-}/ZrO_2	Jatropha seed oil	Catalyst showed high activity at low temperature (40–60 °C) and low catalyst load (2 wt%). The optimum yield 97.91% was obtained by the methanol to oil of 1:8, temperature of 60 °C reaction temperature, 2.15 hrs, and 2 wt% of catalyst load.	97.91 (2.15 h)	[65]
	Soy bean oil	Catalyst showed capability for methanolisis and ethanolisis of soy bean oil. Optimum reaction was 120 °C, 1 h and 5 wt% of catalyst dosage for methanolysis (Yield of 98.6%), and ethanolysis (92%). Molar ratio of methanol: oil = 12: 1.	98.6 (1 h)	[66]
	Croton gratissimus	The biodiesel yield of 90.7 was obtained at 1.5 h of reaction	90.7 (1.5 h)	[67]
	Palm oil	The conversion of 80% for 6 h of reaction was achieved by the use of 1.5% catalyst	80 (h)	[68]
	Neem oil	The conversion of 95% for 6 h of reaction was achieved by 2 h reaction at 70 °C using 1.5 wt% catalyst	95 (2 h)	[69]
	Jatropha curcas oil	The conversions of jatropha oil by methanolysis was 79.7% under conditions of 120 °C, 2 h, 3 wt% of catalyst. Methanol to oil ratio of 4:1.	79.7 (2 h)	[70]
	Jatropha curcas oil	Biodiesel yield of 92.3% was obtained at methanol to oil ratio of 40:1, 65 °C,16 h, and catalyst loading of 12.5 wt%.	92.3 (16 h)	[71]
	Jatropha curcas oil	The yield of biodiesel of 97.9, 60 °C, 3 h and methanol to oil ratio of 8:1.	97.9 (3 h)	[72]
	Jatropha curcas oil	The conversions of jatropha oil by ethanolysis was 59.4%. Ethanol: oil molar ratio of 10:1.	59.4 (500 min)	[73]
	Sun flower seed oil	The highest conversion yield of 90% was obtained under temperature of 100 °C for 4 h, methanol/oil of 9:1 and catalyst dosage of 6 wt%.	90 (4 h)	[74]
	Sea mango seed oil	The highest conversion yield of 83% was obtained under temperature of 180 °C, methanol/oil of 8:1 and catalyst dosage of 6 wt%.	83 (3 h)	[75]
	Oleic acid	The highest conversion yield of 68.5% was obtained under temperature of 60 °C, methanol/oil of 6.1:1 and catalyst dosage of 0.6 wt%.	68.5 (16 h)	[76]
	Myristic	The highest conversion yield of 99% was obtained under temperature of 170 °C, methanol/oil of 20.1:1 and catalyst dosage of 3 wt%.	99 (20 min)	[77]
	Low grade coconut oil	The increasing specific surface area with correlated enhanced catalytic activity.	85 (20 min)	[78]
CoO–NiO promoted sulfated ZrO_2	Waste cooking oil (WCO)	CoO–NiO promoted sulfated ZrO_2 was prepared by co-precipitation method. The catalyst loading of 0.2 wt% for WCO/methanol ratio of 1:3 at 65 °C for 2 h provides biodiesel yield of 98.8%.	98.8 (2 h)	[79]
SO_4^{2-}/ZrO_2-CeO_2	*Jatropha curcas* seed oil	The activation energy of conversion utilizing the catalyst was 45.3 kJ/mol. The maximum conversion of fatty acids was 94.3 % at 8% catalyst loading, methanol to oil volume ratio was 2:1.	94 (1 h)	[80]
Mg-SO_4^{2-}/ZrO_2	Karanja oil	The highest conversion yield of 80% was obtained under temperature of 60 °C during 6–10 h.	80 (6 h)	[81]
SrO/sulfated zirconia	Oleic acid	The acidity of catalysts expressed an important index and a decisive factor of enhanced catalytic activity by SrO doping.	91.1(30 min)	[80]
SO_4^{2-}/TiO_2-ZrO_2	WCO	The increased acidity of catalysts with increasing recyclability was achieved.	96.7 (8 h)	[82]
Ferric-manganese-doped sulfated zirconia)	Sheep fat	Catalyst gave optimimum conditions at catalyst loading of 8 %wt., stirring at 400 rpm for 300 min and temperature of 65 °C.	98.7 (2.5 h)	[83]
La_2O_3/ZrO_2	Sunflower seed	The catalyst with 21 wt% loaded La_2O_3 and calcined at 600 °C showed the optimum activity. The highest yield was 84.9% methanol:oil of 30:1 and catalyst dosage of 5 wt% at the time of reaction of 5 h.		[84]
Bi_2O_3/ZrO_2	Nannochloropsis sp	The loaded Bi_2O_3 elevated both surface acidity and basicity. Highest yield obtained by Bi_2O_3/ZrO_2 which synthesized by using cetil trimethyl ammonium bromide (CTAB), reaction condition of catalyst loading of 20 wt % at 80 °C for 6 h and oil/methanol ratio of 1:90 (g/mL).	73.4 (6 h)	[85]
Isopoly and heteropoly tungstate/ZrO_2	Sunflower seed	The enhanced surface acidity and surface density achieved by the modification. High activity of catalyst was achieved by low catalyst loading (0.2 wt%). The highest yield was obtained by methanol/oil ratio of 20:1, temperature of 200 °C.	92 (5 h)	[86]
WO_3/ZrO_2	Scenedesmus opoliensis	Tungstated zirconia catalyst showed high effectivity as the reaction consumed less time compared to other catalysts. The optimum yield of biodiesel conversion was 94.58% at 100 °C temperature, 12:1 methanol to oil molar ratio and 15% of catalyst amount based on oil weight in 3 h.	94.5 (3 h)	[87]
WO_3/ZrO_2	S. obliquus lipids	The catalyst has amphiphilic superacid property and was prepared by surface modification of SO_4^{2-}/TiO_2-ZrO_2 with n-octadecyltrichlorosilane	96 (5 h)	[88]
Tungstated/ZrO_2	Palm oil	Catalyst exhibited a faster reaction of palm oil conversion using ethanol with activation energy of 51.6 $kJ.mol^{-1}$. A yield of 25% was obtained by the ethanol: oleic acid ratio of 5:1 for 3 h reaction at 50 °C.		[89]
Zirconia-Supported Tungstophosphoric Heteropolyacid	Palmitic acid	The sample with a 30% mass percentage of Tungstophosphoric Heteropolyacid (HPW) has been identified as the most efficient catalyst. The lower loss of activity makes the catalyst efficient as reusable and recyclable catalyst. The catalyst showed a yield of 98% in the first running at 60 °C for 6 h at the methanol to oil ratio of 15: 1, and the yield of 40 % at 5th cycle. The reduced activity is correlated with the catalyst mass loss.	90 (6 h)	[90]
Mo(IV), Cr(III), Ca(II) and Ba (II)	*Milletia pinnata*	The coating was conducted by dip and dry method, The increased catalytic activity and stability of catalyst until 5th cycles was found. The highest	95 (2 h)	[91]

(*continued on next page*)

Table 2 (*continued*)

Catalyst	Oil feedstock	Remark	Maximum Yield (%)/Time of reaction	Reference
		active catalyst was Ca/ZrO_2 which showed a yield of 96% under the methanol: oil ratio of 9, reaction time of 5 h. The yield was insignificantly changed until 5th cycle. The yield at 5th running was 94%.		
Mg/ZrO_2, Ca/ZrO_2, Sr/ZrO_2, and Ba/ZrO_2-	Waste cooking oil	Among the varied metal modifier, the highest activity was achieved by Sr/ZrO_2. The optimum yield was 79.7 % under the catalyst load of 2.7 wt%, 29:1 of methanol ratio to oil, reaction time of 169 min and 115.5 °C.	79 (3 h)	[92]
Sr/ZrO_2	Waste cotton seed oil	The use of catalyst in ethanolysis is beneficial as it requires the lower temperature, lesser alcohol to oil molar ratio, with stability and reusability. A yield of >99% was expressed by the catalyst at the dosage of 5 %wt., methanol to oil ratio of 12:1, reaction time of 7 h and the temperature of 75 °C. The yield decreased to 96 and 85 % for 4th and 5th run, respectively.	greater than99 (75 min)	[93]
CaO/ZrO_2	soybean	Increasing Ca/Zr molar ratio affected to the increasing basicity. The optimum yield was obtained by Ca/Zr = 8/2. The optimum reaction conditions was, methanol/oil ratio of 25:1, catalyst loading of 1.25 wt%, and reaction temperature of 65 °C for 1 h.	98 (1 h)	[93]
CaO/ZrO_2	Palm oil	CaO/ZrO_2 was synthesized by using UiO–66(Zr) and calcium acetate. The catalyst showed higher activity in palm oil conversion under mild condition. The highest active catalyst was obtained by nitrogen activation at 650 °C.	96.99 (1 h)	[94]
CaO/ZrO_2	Low grade coconut oil	The catalyst showed sufficient acidity for faster reaction (20 min). The optimum yield under reaction temperature of 55 °C with 3 wt% catalyst and methanol to oil ratio of 9:1 was 82%.	69.5 (20 min)	[78]
ZrO_2-SiO_2-Me&Et-$PhSO_3H$	Oleic acid	The catalysts of ZrO_2-SiO_2-Me&Et-$PhSO_3H$ were prepared through silication and surface modification with trimethoxymethylsilane and 2-(4-chlorosulfonylphenyl) ethyltrimethoxysilane. The catalyst gave a yield of 82% at 5 wt% catalyst concentration, reaction temperature of 160 °C, 650 rpm speed, and 480 min reaction time	82 (8 h)	[95]
SiO_2@ZrO_2-CaO	Canola oil	Catalyst showed remarkable stability and reusability with high conversion of palm oil. A yield of 83% was produced by using methanol:oil ratio of = 36:1, reaction temperature of 65 °C, ambient pressure, and continuous stirring 300 rpm for 4 h.	80 (7 h)	[96]
Cu–Ni doped ZrO_2	*Capparis spinosa L* seed oil	The catalyst of Cu–Ni doped ZrO_2 appeared highly active, stable, and cheap features for biodiesel industry. Optimum condition of 1:6 ratio of oil to methanol, reaction temperature of 70 °C, reaction time of 1.5 h, and 2.5% catalyst loading produced biodiesel yield of 90.2%.	90.2 (1.5 h)	[97]
*x*Zn/ZrO_2	Litsea cubeba kernel oil	The Zn loading influenced the phase transition from the monoclinic phase to the tetragonal phase with the increase in the Zn loading, along with the enhanced structural stability and thermostability. The highly dispersed Zn species and the $ZnOH^+$ species were the active sites, which could promote this transesterification reaction. Furthermore, the 7% Zn/ZrO_2 catalyst exhibited the best catalytic activity.	97.2 (4 h)	[98]
ZrO_2/SiO_2	Stearic acid	Catalyst prepared by cationic surfactant showed higher activity compared to those synthesized by using anionic surfactant. Catalyst exhibits good reusability till five runs. The catalyst displays suitable recycling as it kept the yield from 85% in the first run to 72.5% at the five recycle runs without significant lack in performance. Reaction condition was at 125 °C for 3 h.	69.2 (3 h)	[99]
SnO/ZrO_2	Soybean oil	The catalyst showed an activation energy of 31.5 kJ/mol for soybean oil conversion.	18 (30 min)	[76]
SiO_2/ZrO_2	Soybean	Nanosized SiO_2/ZrO_2 catalyst prepared by sol-gel method, has surface area of $131.50 \pm 14\ m^2\ g^{-1}$.	96.2 (3 h)	[76]
Sulfated-ZrO_2/SBA-15	WCO	The catalyst was was synthesized by direct impregnation of the synthesized SBA-15 with the desired amount of zirconium hydroxide in mixture with pluronic P123 in HCl solution at 3 h at 40 ∘C to form $Zr(OH)_2$. Tetraethyl orthosilicate (TEOS) was utilized as silica source. The catalyst showed activity by the optimum yield of 95% on the methanol/oil ratio of 1:40, reaction temperature of 140 °C for 10 min.	95 (10 min)	[100]
SO_4^{2-}/ZrO_2–SiO_2(Et)	tripalmitin (Tp) and Eruca Sativa Gars (ESG) oil	The catalyst was prepared by the use of block copolymerization of the framework of SO_4^{2-}/ZrO_2. Bis(trimethoxysilyl)ethane was employed as the ethane bridging agent. The increased acid site amount of the resulting materials is increased. A yield of 82 % was produced by the methanol to oil ratio of 1:5 at the temperature of 65 °C for 24 h.	82 (24 h)	[101]
La_2O_3-ZnO/ZrO_2	Soybean oil	Catalyst showed superbasicity. The optimum reaction condition was methanol/oil = 6 at 70 °C for 12 h	71.3 (21 h)	[102]
GO@ZrO_2–SrO	WCO	Catalyst was synthesized via co-precipitation method by the combination of graphene oxide-bimetal zirconium/strontium oxide nanoparticles. The maximum FAMEs yield of 91% was obtained in the conditions of the material ratio of 1:0.5 (w/w) of GO:ZrO_2-SrO, oil to methanol ratio (1:4), the reaction time of 90 min and the 28 temperature of 120 °C.	91 (90 min)	[103]
ZrO_2/activated carbon	Oleic acid	ZrO_2/activated carbon showed high stability. By the optimization, it was obtained that 99.37% of yield was achieved at the catalyst dosage of 6.76 wt %, molar ratio of methanol to oleic acid of 20.86, and reaction duration of 57.84 min. The yield at the 5th running was 95%.	99.37(57 min)	[104]
Fe_2O_3.MnO-SO_4^{2-}/ZrO_2	WCO	The catalyst showed high yield until six cycle without loss in its activity. The maximum yield of 96.5 ± 0.02% achieved under the optimized conditions	96.5 (4 h)	[105]

(*continued on next page*)

Table 2 (*continued*)

Catalyst	Oil feedstock	Remark	Maximum Yield (%)/Time of reaction	Reference
		of the reaction temperature of 180 °C; stirring speed of 600 rpm, 1:20 M ratio of oil to alcohol and 3 wt/ wt% catalyst loading.		
Li/ZrO_2	Canola oil	Catalyst was prepared by sol-gel method. Basicity is higher compared to Na/ZrO_2 and K/ZrO_2.	98 (3 h)	[106]
$MnO\text{-}NiO\text{-}SO_4^{-2}/ZrO_2$	Palm oil	Catalyst was synthesized using impregnation method. The catalyst has strong acidity 2757.2 μmol/g)	97 (3 h)	[107]
Kalium Hydroxide/Zirconia Pillared Bentonite	Palm oil	The KOH impregnation increased basicity as the catalyst acts as bifunctional catalyst. The optimum catalytic activity produced yield of 81% on the reaction condition of 65 °C for 3 h.	81 (3 h)	[108]
$La_xCe_{1-x}O_{2-0.5x}\text{-}ZrO_2$	Corn oil and WCO	The varied composition expressed $La0.2Ce0.8O1.9\text{-}ZrO_2$ obtained by calcination at 700 ∘C as the effective catalyst. The catalyst with the dosage of 5% wt. exhibited the yield of 92 and 80 % from WCO and corn oil respectively at the temperature reaction of 120 °C, reaction time of 2 h, and the methanol to oil ratio of 15:1.	90 (2 h)	[109]
$SO_4^{2-}/ZrO_2/MCM\text{-}41$	Oleic acid	The surface acidity of catalyst made an efficient optimum condition for the low methanol to oil ratio.	82.6 (4 h)	[110]
Oxophospated zirconia	Vegetable oil	Mesoporous oxo- phosphated sulfated zirconia (m-PSZ) was prepared by sol-gel reaction in the presence of templating agent cetyl trimethyl ammonium bromide (CTAB). The catalyst showed superacidity and expressed a yield of 95.5 % at the reaction temperature of 130 °C for 5 h, methanol/feedstock volume ratio of 1/1 and stirring speed of 400 rpm.	95.5 (5 h)	[111]
Palm Biochar-Based Sulphated Zirconium	Palm oil s	This study achieved a maximum fatty acid methyl ester (FAME) yield of 94.3% and free fatty acid (FFA) conversion of 96.1% via the esterification over 20 wt% Zr-AC-HSO_3 using 3 wt% catalyst concentration, 15:1 methanol: PFAD molar ratio at 75 °C for 3 h.	96.1 (3 h)	[112]
La_2O_3-promoted SO_4^{2-}/ZrO_2	Palm oil	$La_2O_3\text{-}SO_4^{2-}/ZrO_2$ is synthesized using La_2O_3 derived from domestic monazite ore. Catalyst shows stability until 6th cycle. With 20 wt% of La_2O_3-SZ catalyst, the yield of 72 % was obtained under reaction conditions: reaction temperature of 200 °C, catalyst loading of 3 wt%, the ratio of oil to methanol of 1:20. The yield was about 42% at 6th cycle.	75 (1 h)	[113]
Cu–Ni doped ZrO_2	Capparis spinosa L	Catalyst is an efficient and recyclable catalyst. The yield of 90% was achieved at 2.5% wt. of catalyst and temperature of 70 °C.	90 (3 h)	[97]
$K/ZrO_2/gFe_2O_3$	Soybean oil	The catalyst of $K/ZrO_2/g\text{-}Fe_2O_3$ was synthesized prepared by sol-gel method and the material have magnetic properties.	95.6 (3 h)	[114]
cellulose@α-Fe_2O_3–ZrO_2	Lauric acid	The catalyzed reaction gave higher yield compared to the use of $Fe_2O_2\text{-}ZrO_2$.	92.5 (3 h)	[115]
$Mn@MgO\text{-}ZrO_2$	Phoenix dactylifera L. Kernel oil	The catalyst is valued as efficient basic catalyst with 96.4% yield. In addition, the catalyst can be reused for up to six repeated reaction cycles. The economic analysis revealed that biodiesel is produced at 0.46 US $/L on lab scale.		[116]
$HClSO_3$–ZrO_2	palm fatty acid distillate	Catalyst is a superacid catalyst with negligible decrease in the conversion at least for three cycles.	91.5 (3 h)	[117]

of ZrO_2 phase. From the investigation on *Jatropa curcas* seed oil and oleic acid, it is found that the increasing surface acidity obtained at the increasing sulfuric acid concentration [73,118,119] Although the effect of sulfate ions modification on ZrO_2 phase is still controversial, the increasing surface acidity is consistence with the increasing specific surface area. It is associated with the presence of tetragonal crystal phase of ZrO_2 and directly proportional to the pH of precipitation. This behaviour is related to the predominance of OH groups attached to two atoms of Zr (Type II), which less than OH groups attached to three Zr atoms (Type III) in the monoclinic zirconia. This higher OH leads to the higher [73].

Superacidic properties of sulfated zirconia is valued to be more effective compared to sulfated SnO_2 [120]. However, it is also noted that oil feed stock determines the effectiveness of the catalyst. The FAME from feedstock was resulted not only from transesterification mechanism, but also by acid-catalyzed esterification of FFA. Beside of avoiding saponification, it becomes a strategy for faster catalysis. In more detail, the phenomenon of the higher conversion by methanolysis respect to ethanolysis is also fit with general pattern by using other catalysts. As mentioned from *Jatropha curcas* oil conversion, methanolysis gave conversion of 79% meanwhile 59% was achieved by ethanolysis [70,73]. Higher conversion is achievable as confirmed by the higher yield (greater than90%) by optimized catalyst loading to 7.61 wt% [121]. From some literatures, it is conclusively obtained that sulfated zirconia is not feasible for palm oil conversion as less conversion at longer time of reaction and higher oil to methanol ration required compared to the use of other oil feedstocks [122,123].

From Table 2, it can be seen that high yield of more than 90% is generally obtained by methanolysis over sulfated zirconia on various oil feedstock. Compared to the use of KOH as homogeneous catalyst, the use of sulfated zirconia on *Croton gratissimus* oil conversion is similar (90.66–90.70%) with less methanol to oil ratio. The yield values are higher compared to the use of sulfuric acid with optimum condition (80.4%) [124]. From the use of *Jatropha curcas* oil, the superiority of sulfated zirconia was obtained by the higher yield (97.9%) at the same temperature and time of reaction with the use of CaO (94 %) [72].

From the conversion of soy bean oil, it is obtained that catalyst has no good stability due to the surface deactivation after use and the leaching of sulfate and zirconia particles after use. The FAME yields dropped off significantly by recycling, in that from about 99% of yield in first use, the conversion reaches 59, 30, and 14% in the second, third and fourth cycles, respectively [66].

An extra stability of sulfated zirconia was promoted by the combination with nano metals. Ferric-manganese nanoparticles doped onto sulfated zirconia (nano-SZ) enhanced the better reusability [79,125,126]. It is reflected on the use of nano-SZ for tannery waste sheep fat conversion which demonstrated the reusability until 8th cycle of the process. Even though the yield decreased along with the continuing cycle, but the quality of biodiesel from this animal fat met with ASTM D6751standard. Beside of the flash point parameter which slightly higher compared to the standard, other parameters of density, acid number, viscosity, water content and carbon residue are within the

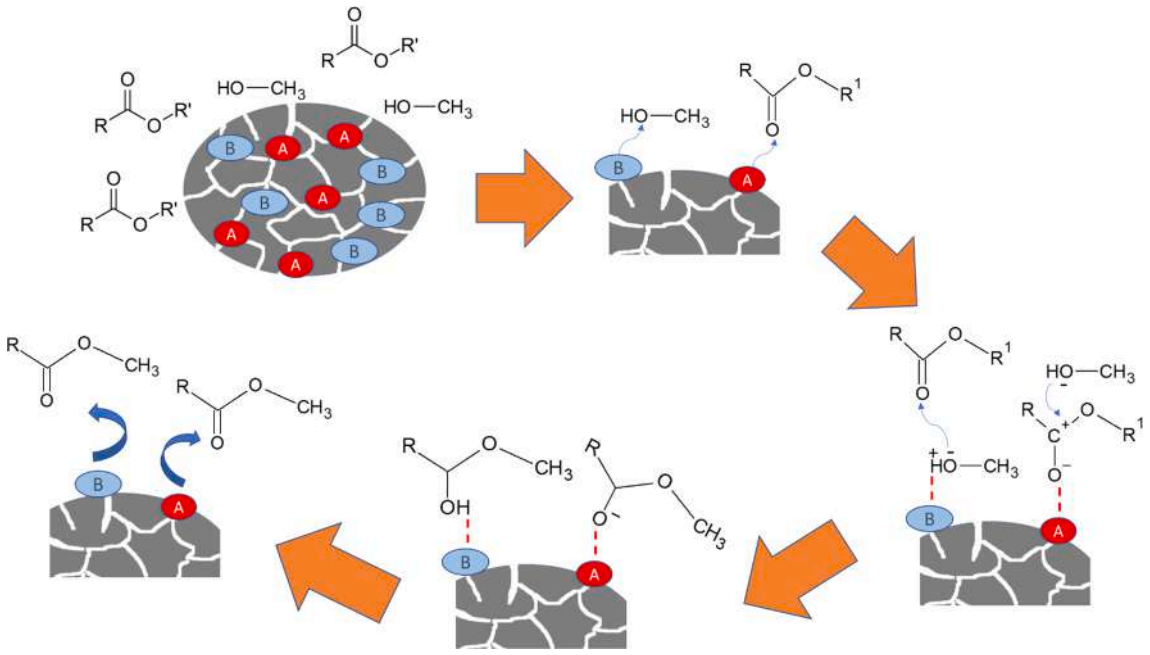

Fig. 9. Bifunctional acid-base catalysis in biodiesel production.

range of the required values[83125]. The stabilized and distinctive enhancement was also reported by the combination with CuO and NiO [79] CeO_2[127], and SrO [126]. Not only the superiority of catalyst in the conversion of WCO until 99% yield, the CuO-NiO/ZrO_2 demonstrated a recyclability until 5th cycles. This beneficial feature is also exhibited by Fe_2O_3-MnO-SO_4^{2-} /ZrO_2 and [105], MnO-NiO-SO_4^{2-}/ZrO_2 [107], and xZn/ZrO_2[98].

The increasing Bronsted acidity was expressed by zirconia-supported isopoly and heteropoly tungstate catalysts. The materials were prepared by suspending a known amount of dried zirconium oxyhydroxide powder in methanol solution of silico tungstic acid (STA) as isopolyacid and polytungstic acid (PTA) as heteropoly acid sources, respectively. The domination of increased Bronsted/Lewis acidity ratio was found at the increased tungstic acid concentration, contributed to the increased yield of biodiesel [86].

The preparation of isopolyacid and heteropolyacid utilizing polyposphotungstic acid was performed by embedding heteropoly phospo tungstic acid (HPW) during the hydrolysis of the Zr(IV) precursor, followed by hydrothermal treatment. Acidic environment was created by protonated ≡Zr–OH groups of the zirconia into $[\equiv Zr–OH_2]^+$, resulting in the formation of electrostatic $[\equiv Zr– OH_2]^+$ $[H_2PW_{12}O_{40}]^-$ pairs by acid-base-like reaction [89,90]. The remarkable competitiveness of the use of these superacid-modified zirconia is the high yield on small amount catalyst loading, and recyclability with insignificant change of activity [86,90,128]. The better reusability compared to sulfated zirconia is attributed to that sulfate ion is easily hydrolyzed in hydrophilic phase, in this case is alcohol phase. From both different reactant in transesterification, it was observed that although heteropoly acids are soluble in polar solvents, a homogeneous accessible acidity was proven by the catalytic activity data [86,101].

The modification with Bi_2O_3 to ZrO_2 represents the increasing not only surface acidity, but also the basicity. In addition, it influenced the particle size, specific surface area, and porosity of ZrO_2. In general, the increasing Bi_2O_3 content enhanced the particle size of both t-ZrO_2 and m-ZrO_2 in the composite, and reduced the specific surface area. It reflects the Bi_2O_3 blocking to the porous structure. The presence of doped Bi_2O_3 with 5% wt. to the ZrO_2 enhanced the surface acidity from 289.14 μmol NH_3/g into 2187.56 μmol NH_3/g at 30% wt. of Bi_2O_3. Meanwhile, from the same comparison, the basicity was increased from 2946.16 μmol CO_2/g into 5150.73 μmol CO_2/g. Even though the porosity decreased, the increasing activity for transesterification was achieved. The faster accessibility of fatty acid molecules on catalyst surface by the more active acid and basic sites was recognized. In this term, the possible mechanism of the reaction can be seen at Fig. 9 [85].

Similar pattern on the increasing both acidity and basicity was also reported by ZrO_2 modification using Mo(IV), Cr(III), Ca(II) and Ba(II) prepared by dip and dry coating methods. The increasing acidity along with the domination of medium and strong acidity and basicity was indicated by the coating. It was not only influenced to enhanced the catalytic activity, but also the stability of the catalyst, as reflected by maintained yield values until 5th cycle of the reaction[91].

The modification of ZrO_2 with alkaline producing Mg/ZrO_2, Ca/ZrO_2, Sr/ZrO_2, and Ba/ZrO_2 exhibited the increased basicity of the material, but along with this, surface acidity was also elevated. The highest activity was achieved by the Sr/ZrO_2 associated with the balanced basicity and acidity. The presence of active sites led to simultaneous esterification and transesterification reactions. Howewer, respect to the high content of FFA in WCO, the yield (79%) is notified as lower compared to the yield by other feedstocks [91]. For examples, the yield of 99% was demonstrated by the use of Sr/ZrO_2 for waste cotton seed oil ethanolysis[44], and about 65% for low-grade coconut oil in short time of reaction (20 min) [78]. In case of CaO/ZrO_2, the basic-catalysis mechanism is preferable with the significant effect of Ca/Zr molar ratio [94,129]. The stability of catalyst was attempted by the combination with Al_2O_3 to form CaO-Al_2O_3/ZrO_2 and SiO_2@ZrO_2-CaO [130,96]. The combination of ZrO2 with Al2O3 tends to produce the porosity and thermal stability[130]. The loaded CaO into the composite at the molar percentage of 0.25 and 0.5 expressed that the incorporation of Ca^{2+} into ZrO_2 lattice led to the formation of a solid solution structure. The structure is effective to maintain the basic sites from being leached in the reaction[131]. High yield of greater than 94% was significant amount for WCO feedstocks [130].

The supporting surface mechanism by creating higher reaction space was attempted by mesoporous composites such as ZrO_2/SiO_2 and ZrO_2/Al_2O_3 [99,125,132]. The creation of mesoporous structure in ZrO_2/SiO_2 was designed by the addition of surfactant as templating agent. Mahmoud et al (2021) examined the use of cationic, non-ionic, and anionic surfactant to the surface properties and catalytic activity for stearic acid

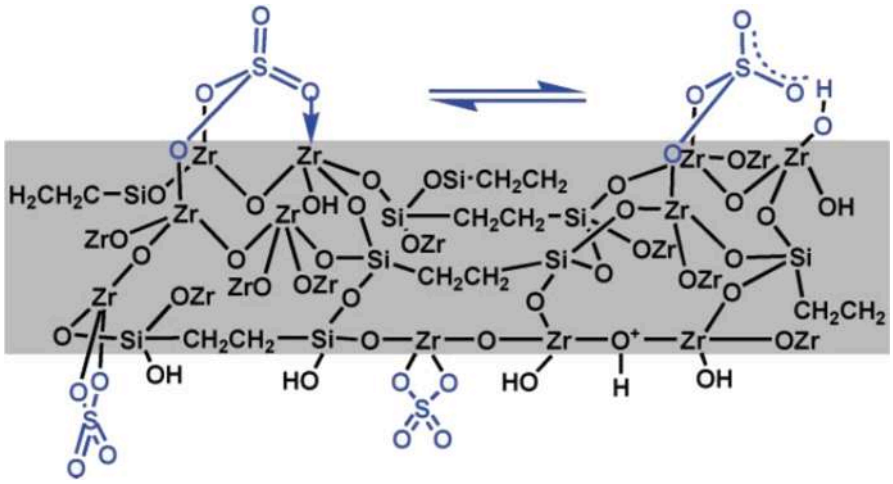

Fig. 10. The structure of ethane-bridged ZrO_2/SiO_2.

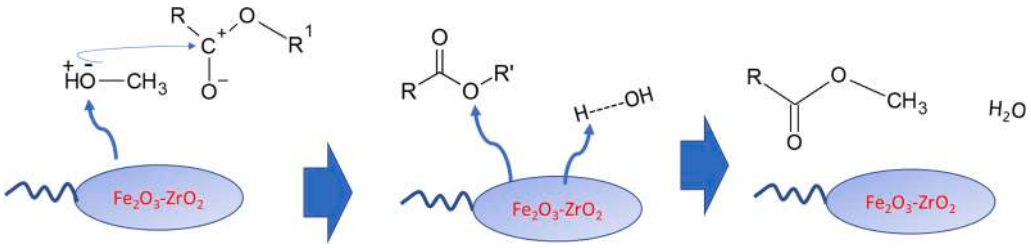

Fig. 11. Transesterification mechanism over cellulose@α-Fe_2O_3–ZrO_2 catalyst [108].

conversion. In addition, the mesoporous ZrO_2/SiO_2 catalysts prepared with cationic (CTAB) and non-ionic (Triton X-100) surfactants demonstrated higher conversion than those with anionic (SDS) or without surfactant [99]. An extremely high specific surface area eas reported by utilization of block-copolymerization in the synthesis of ZrO_2-SiO_2 combined with the sulfation process. Bis(trimethoxysilyl)ethane was employed as the ethane bridging agent, producing a high specific surface area of 839 m^2/g, with the structure of material is presented in Fig. 10 [101].

The ethane-bridged organo-silica moieties into the SO_4^{2-}/ZrO_2 framework results in a combination of well-defined mesoporosity and increased hydrophobicity. This property activates the interaction between triglyceride, and surface followed by a striking enhancement of the transesterification activity. The similar goal was targeted by the combination of sulfated zirconia with defined SBA-15 structure [100]. The catalytic activity towards WCO demonstrated the yield of 96.383% at the reaction conditions of 140 °C, 10 min, and a 1:10 oil-to-methanol molar ratio with a 2.0% catalyst loading [100].

One of other strategies to minimize catalyst blocking and prevent agglomeration of active site is utilization of carbon-based materials such as activated carbon, graphene, graphene oxide and carbon nanotubes [103,104]. The capability of graphene oxide to support the reaction is due to one-layer graphitic product with several hydrophilic functional groups like carboxyl (C=O), epoxy (C-O-C), and hydroxyl (O-H). The combination of surface groups of graphene oxide together with metal or metal oxide nanoparticles play an important role for the effective electrostatic interactions [103]. Similar supportive mode was also obtained by the use of biomass-based material such as activated carbon from palm biochar and other biochar materials [112,133].

An advanced strategy for enhanced kinetics of the reaction was set up by cellulose@α-Fe_2O_3–ZrO_2. The enhanced yield was observed for cellulose@α-Fe_2O_3–ZrO_2 compared to α-Fe_2O_3–ZrO_2, ascribed to the synergetic effects arising upon the hybridization of inorganic nanoparticles with the biopolymer. The catalyst gave a maximum yield of 92.50% after 3 h. The reaction mechanism was by the formation of an activated complex produced from the binding of the catalyst surface and the reactant, and it eliminated the protonation towards methanol. Fig. 11 depicts the predicted mechanism [115].

4. Future prospect and conclusion

From the descriptions of the world's demand on renewable energy source, the potencies, and some examples of the use of ZrO_2-based catalysts, it can be concluded that there are many efforts still required to make sure the applicability of kind of catalyst for industrial scale. Some experiments revealed that various conditions affecting the effectiveness of the catalyst. Even though for same feedstock, the same kind of modified ZrO_2 catalyst can show different activity as shown by different yield. The conclusion was drawn that the catalytic activity of ZrO_2-based catalysts was greatly dependent on the surface profiles consist of surface acidity/basicity, pore structure and specific surface area, and accessible surface by the reactants; in this case, oil and alcohol. The affinity of the surface to facilitate surface reaction was influenced by the texture properties and hydrophobicity. Compared to other catalysts such as CaO, BaO, and MgO for examples, ZrO_2-based catalysts have controllable properties. The condition of less loss during activity is a remarkable feature for reusability and recyclability which are important in the perspective of sustainable and green chemistry [134]. However, the cost for the synthesis of ZrO_2-based catalyst is remarkably higher compared to other catalyst materials such as CaO, natural zeolite, or natural clay minerals [135–137]. Meanwhile, catalyst is only one of some other aspects need to be considered for the life cycle assessment of biodiesel productions. Other aspects consist of the source and cost of feedstock, the land use for a whole process, environmental impact, and the readiness of all subjects in the process. Based on many studies on life cycle assessment (LCA) in biodiesel production [1], elaborating the factors of

oil feedstocks and catalysts is very important. For an example, as the study on microalgae gave a conclusion that it is a promising biodiesel feedstock especially from the perspective of carbon emission, the consideration on its recyclability over various catalysts will give a more comprehensive figure for industry. Based on the basic structure of crystalline ZrO_2, stability and reusability are the advantageous properties to create an adjustable catalytic activity. The combination of controllable feedstock and higher cost-catalyst with better reusability may be another consideration for quality of the product. In other perspective, WCO utilization as major feedstock for production can also be intensively evaluated as part of a circular economy of vegetable oil productions [137].

CRediT authorship contribution statement

Is Fatimah: Writing – original draft, Conceptualization, Validation. **Ika Yanti:** Writing – original draft, Visualization. **Totok E. Suharto:** Visualization. **Suresh Sagadevan:** Writing – original draft, Conceptualization, Validation, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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