

Review

Mesoporous Silica-Based Catalysts for Biodiesel Production: A Review

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Abstract: High demand for energy consumption forced the exploration of renewable energy resources, and in this context, biodiesel has received intensive attention. The process of biodiesel production itself needs to be optimized in order to make it an eco-friendly and high-performance energy resource. Within this scheme, development of low-cost and reusable heterogeneous catalysts has received much attention. Mesoporous silica materials with the characteristics of having a high surface area and being modifiable, tunable, and chemical/thermally stable have emerged as potential solid support of powerful catalysts in biodiesel production. This review highlights the latest updates on mesoporous silica modifications including acidic, basic, enzyme, and bifunctional catalysts derived from varied functionalization. In addition, the future outlook for progression is also discussed in detail.

Keywords: biodiesel; mesoporous silica; catalyst; heterogeneous catalyst



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1. Introduction

Renewable and clean energy is still a very important issue in the world due to declining fossil fuel supplies. In response to this, producing sustainable energy with less CO₂ emission by using biomass feedstock is one of the strategies. In addition, by applying the circular economy principle, biomass feedstock derived from agricultural or forestry cycles can help and enhance food security, environmental security, etc. [1]. As well as reducing global CO₂ emission. Within this scheme, biodiesel is a good alternative due to its huge potential raw material and simple production. In terms of chemical composition and applicability, biodiesel can be a replacement for diesel fuel, which is the petroleum oil fraction containing 8–21 carbon atoms. Originating from different raw material, biodiesel is composed of mono-alkyl esters of long-chain fatty acids derived from various feedstocks such as plant oil, animal fats, or other lipids that are also known as triglycerides. Its composition leads biodiesel to have better performance with respect to diesel fuel, especially in terms of less harmful compounds such as sulfur, less toxicity, and better biodegradability. A life cycle assessment showed a lower CO₂ footprint of by biodiesel than diesel fuel. For example, the reduction in life-cycle greenhouse gas (GHG) is valued as ranging from 40% to 69% compared with petroleum diesel [2,3]. Higher free oxygen in biodiesel results in lower emission and full combustion. However, the corrosion and stability viscosity of biodiesel are still drawbacks of its use. The oxygen-containing compounds such as fatty acids can easily adsorb humidity or react with rubbing surfaces, leading to reduced adhesion between contacting asperities and thereby limiting friction, wear, and seizure. In practical terms, biodiesel harms the rubber parts of machinery [4]. This leads us to recommend the use of biodiesel in a blend with petroleum diesel.

There are numerous techniques that could be used to improve the quantity and quality of biodiesel production from biomass sources such as vegetable oils. Essentially, these depend on the synthesis and quality monitoring of the production, in which esterification and transesterification are the most popular and inexpensive methods. Both esterification and transesterification are alcoholysis reactions, in which, in principle, the ester of triglyceride is converted into methyl ester or ethyl ester by methanol or ethanol as the reactant, and glycerol is produced as a by-product. In addition, esterification converts free fatty acid.

Transesterification is a reversible reaction that can mostly be initiated by the presence of a catalyst. This can theoretically be acid or base catalysis, and in such a situation, simultaneous esterification and transesterification can be performed in a production system. The catalysts can either be in a different phase to the reactant, called a heterogeneous catalyst, or in the same phase as the reactant, called a homogeneous catalyst. The traditional method of transesterification is normally catalyzed using diluted sodium hydroxide as a homogeneous catalyst, which produces a fast reaction but tends to be corrosive. Moreover, recycled waste oils and greases as well as many other low-cost feedstocks usually contain water and are about 10–25% FFA. The existing FFAs could be reacted through saponification, which leads to reduced reaction rates and yields. This is a problem in terms of purification, and to overcome this, an extra pre-treatment step is required in order to meet ASTM biodiesel standards. Apart from these, homogeneous catalysts cannot be recycled and reused, and, moreover, vast amounts of water are required for the washing step. Similar effects are expressed by other homogeneous catalysts such as sulfuric acid or phosphoric acid.

Furthermore, progress towards overcoming these drawbacks has been demonstrated by using solid catalysts as in a heterogeneous catalysis system. The appropriateness of the solid catalyst depends mainly on the composition of triglyceride and free fatty acids (FFAs) in oil or fat, and the reaction condition/system [5]. Although only a small amount in the production system, a catalyst could determine the total cost of production due to its effectivity and reusability in the process. By taking the basic principle of heterogeneous catalysis, a solid catalyst should accelerate a reaction via its capability to adsorb the reactant, for more conducting surface reaction, followed by desorption of the product.

This means that not only is the basicity or acidity of the catalyst surface important, but the solid catalyst should have chemical stability, thermal stability, and high adsorption capacity, mainly for organic compounds. Inorganic solids having porosity and a high specific surface area fit this purpose. Considering the molecular size of triglyceride, alcohol, and the possible products of the reaction, the modifiable pore size, and the possible functionalization of the surface to make it more hydrophobic make mesoporous solids fit the application [6]. On the other hand, the development of catalysts for use in biodiesel production itself has progressed, for example, the use of various types of acid/base catalysts that could be active at room temperature. These were developed and adapted to consider the operational conditions of the reaction with the lowest possible energy. With a similar purpose to the other mechanism, enzyme-based catalysts are also an advancement that is considered fundamental and prospective for the future. This forced modifiable solid supports to be adaptive in terms of catalyst sustainability [5,7].

Inorganic synthetic and natural solids such as metal oxide, mixed noble metal oxide composites, zeolite, clay, carbon, silica, silica alumina, and their modified forms have been reported. Among these materials, mesoporous silica-based catalysts demonstrated a superiority for biodiesel production. Based on the progress of published papers, an increasing amount of research on mesoporous silica-based catalyst is demonstrated, as can be seen from the comparison presented in Figure 1.

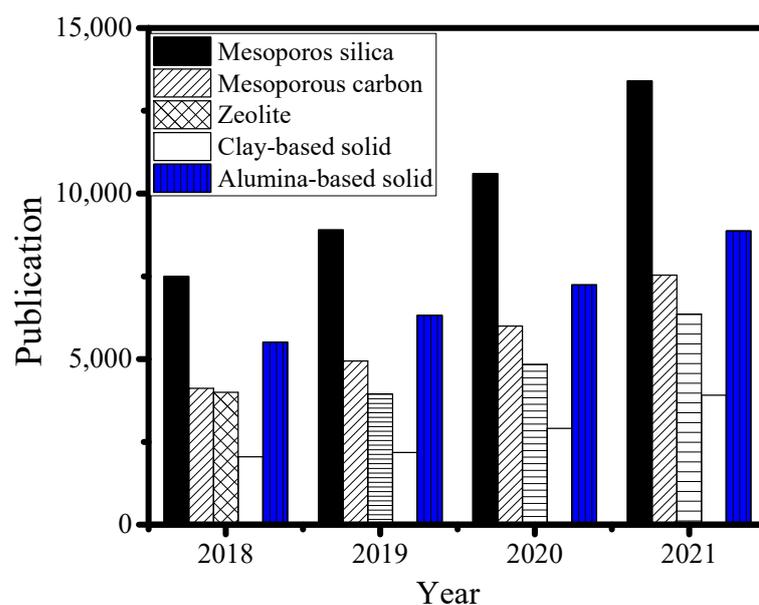


Figure 1. Popularity of mesoporous silica-based catalysts for biodiesel production [Source: SCOPUS database, February, 2023].

The intensive interest in mesoporous silica-based catalysts is expressed by the increasing number of published papers ranging from 2018 to 2021. Individually, the objectives are higher compared to the published papers on mesoporous carbon, zeolite, clay, and alumina-based solids catalysts [8–11]. These indicate the superiority, potency, and possible intensification of mesoporous silica-based catalysts. Some highlighted features of mesoporous silica-based catalysts in biodiesel production are correlated with the tunable porous size and structure and easy embedding of functional groups consisting of either acid/base sites or the hydrophobic/enzymatic sites. Referring to these objectives and publication progress, this review studied the bigger picture of the development of mesoporous silica-based catalysts for biodiesel production, potency, and future challenges in depth [12–14]. The study will begin with the kinds and classification of mesoporous silica materials, modified mesoporous silica in terms of biodiesel production mechanisms, and, furthermore, some possible challenges that need to be overcome and explored for future industrialization.

2. Various Types of Mesoporous Catalysts

Mesoporous catalyst materials have a well-defined pore network with sizes ranging from 2 to 50 nm. This mesoporous material exhibits a unique pore structure with interconnected voids and channels, giving it porosity and a large surface area. Various mesoporous catalyst materials have been developed, including mesoporous carbon materials, metal oxides, metal organic frameworks (MOFs), and mesoporous silica (MCM-41 and SBA-15). These materials have characteristics depending on the raw materials and synthesis methods used. Several previous studies have reported various metal oxides as fillers for mesoporous materials such as Al_2O_3 , ZrO_2 , TiO_2 , and ZnO_2 , showing good performance as catalysts due to their high firmness and low temperature deposition capacity [15]. Apart from metal oxides, a mesoporous material that has been widely developed and used as a catalyst in the biodiesel process is mesoporous carbon material. Mesoporous carbon provides a large surface area and uniform porosity, so it has a high absorption of long FFA chains during the conversion process [16]. However, the catalytic performance of this material is affected by the modification or functionalization of the functional groups on its surface. Several methods, such as chemical and electrochemical reduction, can be used to achieve this modification. Apart from these two types of mesoporous materials, mesoporous MOFs are promising in the catalytic process of biodiesel production. MOFs are a class of crystalline

materials consisting of metal ions or clusters coordinated with organic ligands. These materials have a highly ordered structure with an orderly arrangement of metal knots or groups interconnected by organic linkages, forming a three-dimensional framework. MOF fabric has a high surface area and porosity, so it is very suitable as a catalyst. However, this material still has disadvantages such as low stability, a complex synthesis process, and, in some cases, the larger pores in the mesoporous MOFs can be blocked or inaccessible to molecules, reducing mass transport efficiency and inhibiting the material's catalytic activity or adsorption capacity [17]. The latter is a mesoporous silica material with a hexagonal structure with several prominent properties, such as high porosity, thick pore walls, and high thermal stability. Compared to metal oxide catalysts and others, using mesoporous silica as a catalyst in biodiesel production offers several advantages, such as high surface area, modifiable pore size and structure, good thermal stability, acid–base versatility, and low cost or availability of raw materials. For example, mesoporous silica catalysts can be modified to have different acidic or basic properties depending on the specific reaction requirements. This versatility makes it possible to adapt the trigger's properties to the particular conditions of the biodiesel production process, such as esterification or transesterification reactions. Metal oxide catalysts usually have a fixed acidity or basicity, limiting their flexibility [18]. Silica-based catalysts are generally more cost-effective due to the abundance of raw materials, making them easier to obtain for synthesis and commercialization than metal oxide-based catalysts.

3. Mesoporous Silica Materials and Modified Forms

Mesoporous silica is an inorganic polymer nanomaterial having a high specific surface area and specifically with a pore size ranging from 2 to 50 nm. In principle, mesoporous silica is synthesized through a controllable polymerization of silica precursors, mainly based on the Stöber method [19]. Typically, the synthesis mechanism involves the hydrolysis and condensation of silanes in basic, acidic, or neutral aqueous solution, called sol–gel processes. Such techniques with various methods of polymerization, the use of surfactant or template, and other specific conditions of sol–gel mechanisms were applied to achieve a uniformly adjustable pore size and highly ordered channel structure [20]. From these synthesis conditions, an impressive diversity of synthesis approaches have been developed and patented and now well-established for specified mesoporous silica materials. In 1992, a new family of mesoporous material was synthesized by Mobil Oil Company, and then called MCM-41. The material has a homogeneous ordered pore size distribution ranging between 2 nm and 10 nm, and went on to form the basis of developing cubic-MCM-48 and lamellar-MCM-50. These pioneering findings were followed by various kinds of mesoporous silica materials such as Michigan State University (MSU-1), hexagonal mesoporous silica (HMS), Technische Universiteit Delft (TUD), Santa Barbara Amorphous (SBA), Meso Cellular Form (MCF), etc. [21–23].

Based on the synthesis mechanism, it can be concluded that there are some crucial factors that determine the pore size distribution and ordered structure, i.e., the rate and mechanism of polymerization, gelation mechanism, and the presence of surfactant, co-surfactant, solvent, and co-solvent types. The surfactant influences the pore size distribution due to their molecular size, hydrophobicity, and ionic/non-ionic state [19].

The highly specific surface area of mesoporous silica materials provides potential for various heterogeneous catalysis applications. From a green chemistry perspective, some mesoporous silica materials can be prepared using low-cost raw materials such as clay (bentonite, kaolinite), fly ash, and bottom ash [13,24,25]. Regarding the surface catalysis mechanism, specific features such as pore size can be adjusted according to the type of material. Moreover, special characteristics required in catalysis such as surface acidity, basicity, or the strength of certain molecular interactions can be achieved by modifying the surface of the material. The attachment of certain functional groups to the surface can be carried out based on the surface properties of the material, which is rich in hydroxyl groups. The modification can be physical or chemical modification. Physical modification is mainly

performed through adsorption, wrapping, and other physical effects. Meanwhile, chemical modification commonly utilizes the Lewis acidity–basicity interaction between the coupling agent containing organic functional groups. Through this mechanism, functional groups such as -SH, -NH₂, -Cl, or -CN could be tethered onto the surface via a grafting functional group [8,26,27]. Figure 2 represents the simple mechanism of sulfonic acid tethering on mesoporous silica's surface to enhance the surface acidity for the transesterification reaction.

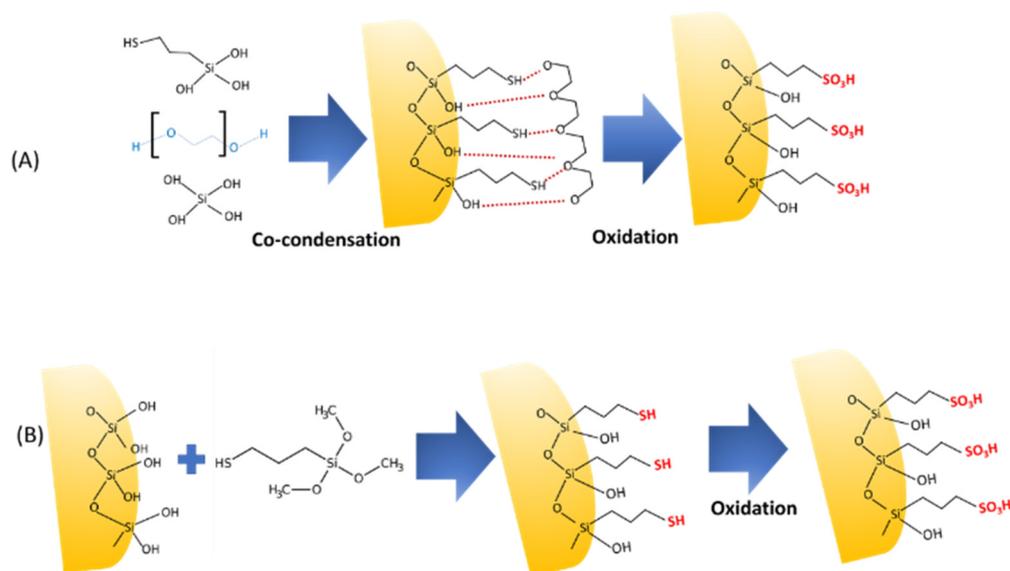


Figure 2. Scheme of sulfonic acid tethering onto mesoporous silica through (A) co-condensation and (B) post-synthesis methods.

Generally, there are two main mechanisms for surface modifications: the simultaneous/co-condensation sol–gel process and post-synthesis methods. Co-condensation is a one-step synthesis method in which the organic, acid/base, or enzyme precursor is added into the reactant of silica polymerization. With different steps, in the post-synthesis, the functional groups are tethered or anchored onto the silica surface after the mesoporous structure is created. Figure 2 describes the mesoporous silica functionalization by an SO₃H functional group through the co-condensation and post-synthesis methods [28,29]. According to several works [29–32], both methods result in SO₃-functionalized mesoporous silica with enhanced surface acidity, acid catalysis capability, and reusability for biodiesel production without any significant difference. However, somehow, the features could be remarkably different for other functionalizations. In the next part, a description of the kind, method, and specificity of functionalized mesoporous silica as a catalyst for biodiesel production is discussed. The discussed functionalization is classified into: (i) acid or base surface functionalization; (ii) metal or metal oxide supporting; (iii) ionic liquid functionalization; and (iv) anchoring enzymes on the surface of mesoporous silica.

3.1. Acid- or Base-Functionalized Mesoporous Silica

For the transesterification and esterification mechanisms in biodiesel production, both acid and base catalysts could be employed. Acid surface functionalization onto mesoporous silica is performed through the attachment of sulfonic acid, organo-sulfonic acid, phosphoric acid, tungstophosphoric acid, etc. Meanwhile, basicity enhancement by attaching an alkaline earth base and alkylamine functionalizations are the strategies that have been reported. In many kinds of catalysis, sulfonic acid and amine modifications are the most common functional groups introduced onto mesoporous silica. Sulfonic acid-functionalized MCM-41, SBA, MCM-48, and KIT are some examples in this scheme, and, specifically for biodiesel production application, Table 1 lists the details of the acid

functionalization method and the impact of the functionalization on the catalytic activity in biodiesel production.

A series of organosulfonic acid-functionalized SBA for the transesterification of soybean oil was reported in [33]. The organic sulfonic acids are propyl-sulfonic acid (Pr-SO₃H), arene-SO₃H (Ar-SO₃H), fluoro-sulfonic acid (F-SO₃H), and modified arene-SO₃H. Except for F-SO₃H and modified arene SO₃-H functionalization, the organosulfonic acid-SBA 15 samples were prepared using co-condensation methods. Tetraethyl orthosilicate (TEOS, 98%, Aldrich) was used as silica precursor in the synthesis, and for the Pr-SO₃H and Ar-SO₃H functionalizations, (3-Mercaptopropyl) trimethoxy silane (MPTMS) and 2-(4-chlorosulfonyl phenyl) ethyltrimethoxy silane (CSPTMS) were utilized as the anchoring agent before oxidization into organo-sulfonic acid conversion. The post-synthesis of F-SO₃H-SBA-15 was performed by interacting perfluorosulfonic acid precursor with calcined SBA-15 (refer to previous investigation [34]). Meanwhile, the Ar-SO₃H was then furthermore modified through a reaction with methoxytrimethyl and methylation to obtain modified Ar-SO₃H-SBA-15. The surface acidity of the materials was assayed through potentiometric titration using TMA as the basic standard solution. Details from the surface acidity measurement revealed that there is a significantly increased exchange of TMA with the modification. The surface acidity is relevant with the increased yield of soybean transesterification by using butanol over a microwave-assisted reaction. Among the organosulfonic acids, F-SO₃H-SBA-15 was the most superior catalyst as it produced about 80% of butyl ester in a short time. However, the recyclability of the catalyst is still an important issue to be resolved as the catalysts lost their activity after first usage. This is demonstrated by F-SO₃H-SBA-15, in which the catalyst could not be regenerated. The surface acidity seems to be diluted in the reaction system. A similar phenomenon of the superiority of F-SO₃H-SBA-15's catalytic activity was demonstrated in the methanolysis of palm oil, in comparison with the activity of Pr-SO₃H-SBA-15 and Ar-SO₃H-SBA-15. In addition, the Ar-SO₃H-SBA-15 showed recyclability until the third use without any significant yield reduction [34]. Similarly, SO₃H-HM-ZSM-5 exhibited excellent improvement of oleic acid conversion until 100% at a low temperature of reaction (88 °C) [35].

From several studies presented in Table 2, it can be summarized that the surface acidity and pore distribution of functionalized mesoporous silica are more important for determining catalyst activity and yield than the hydrophobicity character [36,37]. Although, in general, sulfonation tends to decrease the specific surface area of mesoporous silica materials, a significant enhancement of surface acidity was expressed by post-synthesis sulfonic acid functionalization onto MCM-48, MCM-41, KIT-6, and SBA-15 [38,39]. The significant role of surface acidity is also reflected by the reduction in activation energy (*E_a*) caused by aryl sulfonic acid functionalization, which referred to acid stabilization rather than the hydrophobicity and specific surface area [40]. However, sometimes, the compared physicochemical characterization highlighted that the specific surface area data are in line with the order of surface acidity. Both characteristics are proportional with the catalytic activity, so the conversion and yield are in following order: SO₃H-MCM-48 > SO₃H-MCM-41 > SO₃H-SBA-15. According to a more detailed assay using NH₃ temperature program desorption (NH₃-TPD), the materials are rich in low acidity, as identified by the release of protons at temperatures ranging from 100 to 350 °C. The acidity fits with the optimum reaction for palmitic acid, which lay at around 160 °C. A comparative study on the type of organosulfonic acid was performed by evaluating propyl sulfonic acid (Pr-SO₃H), phenol sulfonic acid (-PhSO₃H), and the methyl- and hexyl-grafted phenol sulfonic acid SBA and MCF [41]. Remarkably, it is noted that the grafting for hydrophobicity enhancement does not effectively increase the conversion and selectivity, but it tends to maintain the stability of the catalyst, at least for a second catalytic run [34,42].

In the co-condensation preparation of propylsulfonic acid (PrSO₃H)/KIT-6, the PrSO₃H content affects the pore expanding. As the pore accessibility becomes rate-limiting in the esterification of long-chain fatty acids such as lauric and palmitic acids, the increasing pore size by sulfonic acid attachment improved the turnover frequency until 70% [43]. A

more simple procedure to enhance surface acidity was expressed by the heteropolyacid ($H_3PW_{12}O_{40}$)/(HPA) impregnation of mesoporous silica structure. An increased conversion of palmitic acid was demonstrated by HPA/MCM-41 [44]. The catalyst showed 100% conversion toward palmitic acid and a turnover number of 1992. It is also important to note that the catalyst is easily recyclable, without any activity change until the fourth cycle.

A study on the preparation of HPA-impregnated KIT-6 (HPA/KIT-6) with varied content (10, 20, and 40 wt%.) as a catalyst for neem oil transesterification revealed the significant improvement in yield, conversion, and reusability of the catalyst, which was related to the presence of surface acidity in the composite. With a similar objective, a study on HPA immobilization in MCM-48 was also performed with the content ranging from 0 to 50% for palmitic acid transesterification using cetyl alcohol [45]. The combination of Lewis and Brønsted acidity influencing the conversion of oleic acid was reported for zirconium-doped MCM-41-supported WO_3 . This depends on the WO_3 loading, ranging from 15 to 25 wt%. The better WO_3 dispersion supports the activity and stability at high temperatures [46]. High conversion was maintained at 97% even in the condition of the presence of 5.5 wt% of water, suggesting that water is not adsorbed on the active centers of the catalyst and oleic acid molecules.

However, it is not only surface acidity that influences the optimum conversion, but the fine dispersion of small clusters of HPWA on the catalyst surface also plays a significant role. The surface area and pore distribution do not linearly respond to the HPA content, but an optimum is reached at about 15 wt%. [47]. A similar effect on the increased pore distribution, where the increasing pore accessibility of the fatty acid led to optimum surface reaction of canola oil transesterification, was represented by HPA immobilization on aluminophosphate [47]. A similar trend was reported for the comparison of HPA dispersion onto MCM-48, which showed the order of catalytic activity was as follows: MCM-48 > SBA-15 > MCM-41. The higher activity is correlated with the structural geometry of the pores [48]. Furthermore, the combination of sulfonic acid and HPA expressed a synergistic effect, enhancing the activity and hydrothermal stability of the mesoporous silica [49].

Table 1. Various acid/base-functionalized mesoporous silica for transesterifications.

Catalyst	Preparation Method	Transesterification Reaction	Remark	Reference
Ar-SO ₃ H/SBA-15	Aryl-sulfonic acid-functionalized SBA-15 material was synthesized by following the one-step co-condensation procedure.	Crude soybean oil transesterification	Catalyst showed recyclability until third use without any significant yield reduction. Arene structure gave higher surface acidity and tends to give better catalyst stability.	[34]
SO ₃ H/SBA-15	SO ₃ H/SBA-15 was prepared through the co-condensation method.	Olive pomace oil transesterification	Increased conversion of oleic acid was reported. The catalyst has reusability properties.	[36]
Propyl sulfonic-KIT-6	KIT-6 silica functionalized with sulfonic acid through the co-condensation method.	Cashew nut oil transesterification by butanol	The KIT-6 propylsulfonic acid catalyst was able to produce a 70% butyl ester yield.	[39]

Table 1. Cont.

Catalyst	Preparation Method	Transesterification Reaction	Remark	Reference
SO ₃ H/MCM-41	Material was prepared by using polystyrene as a template and p-toluenesulfonic acid (TsOH) as a carbon precursor and –SO ₃ H source.	Oleic oil transesterification	Catalyst showed recyclability until fifth use without any significant conversion reduction.	[37]
Propyl sulfinic-KIT 6	KIT was prepared by using pluronic acid P123: TEOS: BuOH:HCl:H ₂ O = 0.017:1:0.31:1.83: 195. After calcination, silicas were functionalized with sulfonic acid groups by post-grafting using mercaptopropyl trimethoxysilane (MPTS 95%) and the thiol was converted by oxidation using H ₂ O ₂ .	Propanoic and hexanoic esterification	The enhancements in turnover frequency (TOF) toward propanoic and hexanoic acid esterification were 40 and 70%, respectively.	[43]
12-Tungstophosphoric acid anchored to MCM-41	MCM-41 was synthesized through the sol-gel method using surfactant cetyl trimethyl ammonium bromide (CTAB), NaOH, and TEOS. 12 Tungstophosphoric acid (12-TPA) was impregnated by stirring at 100 °C for 10 h.	Transesterification of palmitic acid	The catalyst shows high activity in terms of 100% conversion toward palmitic acid and a high turnover number of 1992.	[44]
12-TPA/MCM-48	MCM-48 was prepared through the sol-gel method with composition of 1 M TEOS: 12.5 M NH ₄ OH:54 M EtOH: 0.4 M CTAB: 174 M H ₂ O. 12-TPA was impregnated by incipient impregnation.	Transesterification of jatropa oil (JO)	The uniform dispersion of HPA inside the 3D channels of MCM-48 influenced the increasing activity for the esterification of oleic acid under mild conditions. The catalyst could be used for biodiesel production from WCO and JO with very high conversion: 95% and 93%, respectively.	[48]
HPA/KIT-6	KIT-6 was synthesized through hydrothermal condensation using precursor at a molar ratio of 1 TEOS: 0.017 P123:1.83 HCl (35%):1.3 n-BuOH: 195 H ₂ O. HPA functionalization to KIT-6 was conducted by impregnation.	Transesterification of neem oil	The conversion of neem oil depends on Brønsted acid sites, large surface area, pore size, and the fine dispersion of HPA in the composite. The optimum HPA content in the composite is 20%.	[50]
1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD)/SBA-15	SBA-15 was prepared using a P123 templating agent. 1,5,7-triazabicyclo [4.4.0]dec-5-ene [TBD] was functionalized through the adsorption method in a nitrogen environment.	Transesterification of soybean oil	The higher the grafted base amount, the higher the FAME yield.	[51]

Table 1. Cont.

Catalyst	Preparation Method	Transesterification Reaction	Remark	Reference
TBD/MCM-41	Material was prepared through the post-synthesis method. TBD was anchored by immersing MCM-41 in TBD using tetrahydrofuran (THF) as a solvent, followed by filtration.	Transesterification of soybean oil	The TON was 57, higher than that of MCM-41 (48). The catalyst is reusable.	[52]
Piperazine/MCM-41	Material was prepared through the post-synthesis method. Piperazine was anchored by using the reflux method in dry toluene and propylamine in a N ₂ atmosphere.	Transesterification of soybean oil	The TON was 1270, higher than that of MCM-41 (48). The catalyst is reusable without any activity loss in the second cycle.	[52]
Amine-functionalized SBA-15 and MCM-41	Material was prepared through the post-synthesis method. Amine functionalization was conducted by grafting in anhydrous toluene under argon.	Transesterification of glyceryl tributyrate	The aniline-functionalized OMS materials display the highest conversion in transesterification.	[53]
Diphenylamine(DPA)/SBA-15 and DPA/MCM-48	Material was prepared through the co-condensation method.	Transesterification of oleic acid	Diphenylammonium salts were immobilized onto meso-porous silicas using either the co-condensation or grafting technique. The resulting catalysts were highly effective at esterifying the FFA in greases (12–40 wt% FFA) to FAME but displayed only minimal activity in transesterifying glycerides.	[54]
Sulfonated phosphotungstic acid-modified ordered mesoporous silica (HPW/OMS-SO ₃ H)	HPW/OMS-SO ₃ H was prepared through the co-condensation method in non-hydrochloric acid solution.	Transesterification of oleic acid	The catalyst showed very high hydrothermal stability and recycling performance. The reaction catalyzed by 0.3HPW/OMS-SO ₃ H-5 followed pseudo-first-order kinetics, and E _a was found to be 22.46 kJ/mol.	[49]

The surface basicity modification of mesoporous silica is usually performed by anchoring alkylamine and other nitrogen ligands, and the immobilization of alkali/alkali earth oxide such as CaO, MgO, and Li₂O [45,52,53,55]. The modification of mesoporous silica with 3-aminopropyltriethoxysilane (RNH₂), 2,3-aminoethylamino)propyltrimethoxysilane (NN), and 3-diethylaminopropyltrimethoxysilane (DN) showed increased basicity, which related to the increasing turn-over number. The compared kinds of amines confirmed the superior performance of the tertiary amine [56]. The presence of tertiary amines can also facilitate an increase in nucleophilicity due to the presence of three alkyl groups, making the catalyst more reactive and able to form more robust interactions with the reactants

during the transesterification process. This process causes faster kinetics and increases efficiency compared to secondary and primary amines.

SBA-15 immobilized with 1,3-dicyclohexyl-2-octylguanidine (DCOG) was prepared due to the fact that guanidine compounds are strong bases with higher basicities comparable to carbonates and alkali hydroxide [51,57,58]. The preparation involved the covalent attachment of DCOG onto the SBA15 surface, which increased the solid basicity and recyclability [58,59]. With the similar reason of the strength of basicity, 1,5,7-triazabicycloij[4.4.0]dec-5-ene (TBD) and 1,1,3,3-tetramethylguanidine (TMG) were used to functionalize SBA-15 and MCF [41,51]. A study on TBD functionalization to SBA-15 showed that the higher the amount of TBD grafted to SBA-15, the higher the FAME yield obtained, even though the SBA-15 support does not express the activity. Conversely, the free TBD base is extremely reactive, as a complete trans-esterification into FAMEs was observed after just 1 h of reaction.

From the study, the functionalized materials became active at lower reaction temperatures, and the activity is greatly influenced by the support. The activity is closely related to the surface basicity, which results from the stability of the cations playing a role in the catalysis mechanism. Similar to the result of [56], the catalytic activity is related to the stability of cations caused by the delocalization of the positive charge on the electronegative nitrogen atoms, and also the possible resonance. In line with this finding, the superiority of guanidine-modified MCM-41 with respect to the piperazine-modified sample was reported. The turnover number (TON) of guanidine-modified MCM-41 in the soybean oil transesterification was 1270, while that of piperazine-MCM-41 was 57. A comparison of the modifiers, presented in Figure 3, shows the superiority of aniline-functionalized ordered mesoporous silica (OMS) [53]. However, when comparing mesoporous silica functionalized with aniline and tertiary amine, the sample functionalized with aniline has a more substantial base site and has higher basicity than the tertiary amine. Basicity is very important in the transesterification reaction. After all, it helps activate the alcohol in the conversion to biodiesel. In addition, mesoporous silica functionalized with aniline has a large pore size, which allows for increased accessibility of the reactants into the active site of the catalyst [60].

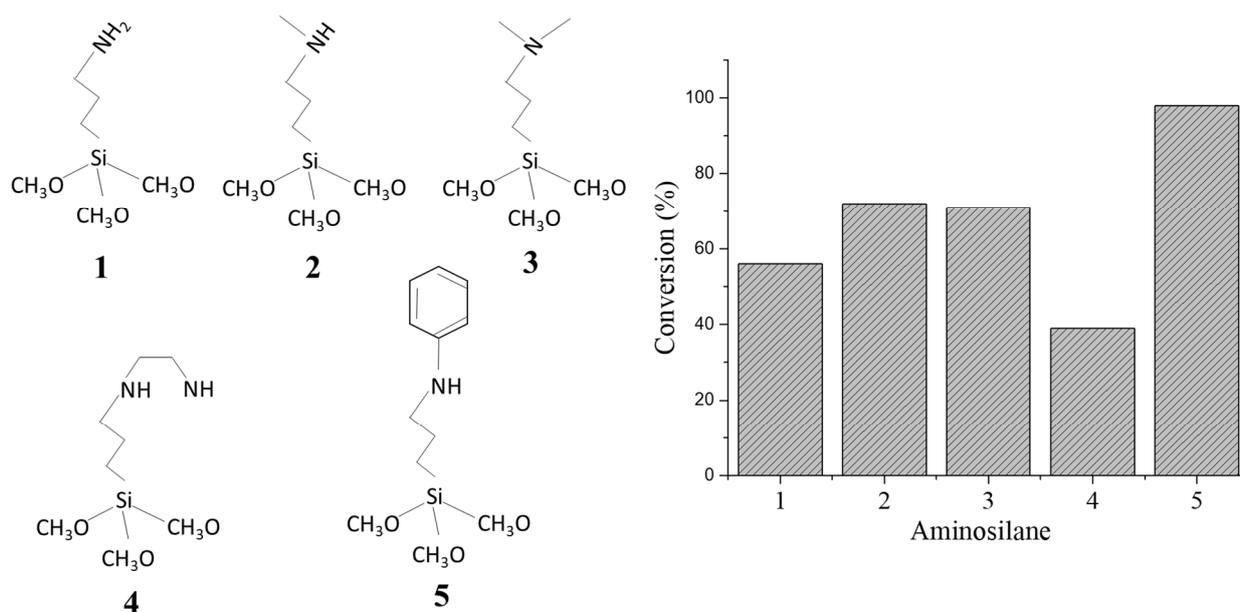


Figure 3. Comparison on the amine modifier n transesterification conversion.

The loss of activity becomes an important issue of acid/base-functionalized mesoporous silica. According to some papers, the reduced activity is mainly caused by the blocking solid porosity and the leaching of the active phase. One interesting case was

expressed by guanidine-modified MCM-41, in which the conversion decreased significantly from 99% in the first use to 86% and 26% in second and third usage, respectively. An investigation on the possibility of guanidine leaching indicated that the anchored functional group is still maintained. ^{13}C CP/MAS NMR analysis of the catalysts demonstrated that the decreased catalytic activity was caused by the neutralization of the basic sites by the free fatty acids present in the oil. The binding causes catalyst poisoning [52]. In addition, the leaching of non-chemically bonded amine groups is the main reason for the loss of activity after recycling. Other factors include the non-intensive interaction between bulky surface and triglyceride, which leads to the tendency to be more active for converting free fatty acids (FFAs) [54]. Recyclability is achievable by the combination of acid/base-functionalized magnetic mesoporous silica [61] and is similarly reported for other modifications such as enzymes and metal/metal oxide [61,62].

3.2. Metal- or Metal Oxide-Impregnated Mesoporous Silica

Adding metal species or metal oxides to mesoporous silica can produce new properties and functions, especially for catalyst applications. The synergistic combination of mesoporous silica's high surface area and pore structure with the catalytic properties of metals or metal oxide species opens opportunities for advanced materials with tailored functionality and enhanced performance. The choice of metal modification or metal oxide for mesoporous silica is application-dependent. As a catalyst for biodiesel production, the catalytic activity and stability of the material will be affected by the type of metal or metal oxide modified on the surface of the mesoporous silica. Therefore, further studies and literature reviews related to comparing the use of metal or metal oxides need to be conducted. Other than amine functional groups, impregnating CaO, MgO, and Li_2O into mesoporous silica materials are also popular methods for improving total basicity and the yield of biodiesel. Impregnation is a simple method to disperse the alkaline earth oxide. Table 2 presents some metal/metal oxide-modified mesoporous silicas and their performance in biodiesel production. In general, the dispersion does not affect the structure of the mesoporous silica much but generally reduces the specific surface area of the material. The high total basicity, homogeneous dispersion of metal oxide, particle size, and strong interaction between support and metal oxide determine the conversion. This is reflected by the higher activity of CaO/SBA-15 compared to CaO/MCM-41 [63]. In order to achieve a homogeneous distribution of Ca in the structure of the nanocomposite, a synthesis route can be taken by including calcium acetate or calcium citrate in the silica gel hydrolysis [64]. From the range of studies, it can be concluded that the modification of basicity or acidity in mesoporous silica significantly influences the catalytic activity and reusability of the catalyst, but the main factor in increasing the features is the character of the support. The specific surface area of the mesoporous silica determines the possibility of functional organic molecules blocking the solid pores, but, on the other hand, changes the surface hydrophobicity.

Even though the study on MgO dispersion into various mesoporous silicas such as MCM-41, KIT-6, and SBA-15 revealed that the characteristics of the host such as surface area, basicity, and porosity are important for the conversion enhancement, as well as the surface Mg concentration, the improvement in the catalyst activity seems to be from the combined effects of the multiple attributes of its host material and metal oxide distribution [65,66]. This shows that the activity of a base catalyst does not predominantly depend upon its basic properties. As an example, the stability of MgO/ZSM-5 is recognized as an important parameter to ensure the reusability of the catalyst, as the yield of biodiesel produced from *Spirulina* oil was still above 85% until the fifth cycle. The conversion obeys pseudo-first-order kinetics with the activation energy of 49.67 kJ/mol [67]. It is also important to note that mesoporous silica itself does not show any catalytic activity for the reaction. Within the scheme of enhancing surface acidity/basicity, supporting metals and metal oxides added onto mesoporous silica materials are well-known active catalysts for various reactions. Similar to the functional group modification, in principle, the supporting procedure could be

the incorporation of metal into the framework of mesoporous aluminosilicates to improve the acidity and, in the other method, the impregnation of metal or metal oxide.

Various metal and metal oxides such as W, Ce, Zr, Ca, Mo, and Zn were reported as the active site for biodiesel conversion from many plant oils [68,69]. In addition, the combination of both methods for bimetal-modified mesoporous silica has also been attempted. For example, Ce/Al-MCM-41 and Zr/Al-MCM-41 were prepared through the impregnation of Ce and Zr metal precursor into Al-MCM-41, which was directly synthesized through the sol-gel method of Si and Al precursors [70]. In the case of Al-MCM-41, Al-MCM-48, or Al-SBA-15, for example, the precursors are usually transformed via alkali fusion in the hydrothermal condition with the presence of surfactant as a templating agent [71–75]. The isomorphic substitution of silica with alumina improves the Brønsted acidity of the mesoporous sample, and the presence of the ionic charges of the structure means there is potential to be replaced with metal or metal oxide precursors. As-synthesized Ce/MCM-41 shows extreme improvement for sunflower conversion into biodiesel with respect to the homogeneous distribution of Ce in the structure, as the identified agglomeration leads to the reduced conversion.

In addition, the reusability of Ce/MCM-41 is an important feature with respect to the pristine MCM-41, in which loss of the activity is easy [76]. The loading of active metals such as Ce, Ca, Ti, and Zn onto Al-MCM-41 or other mesoporous materials support could be performed various intensification methods. One of these is ultrasound irradiation [76,77]. The Ca dispersed into Al-MCM-41 demonstrated the significant effect of ultrasound-assisted dispersion on the uniformly distributed Ca in the nanocomposite [70]. A similar result was reported for ultrasound-assisted Zr dispersion and the sulfation of Zr/MCM-41. The irradiation of ultrasonic waves during sulfuric acid impregnation over Zr/MCM-41 improves the morphology, particle size, surface area, and particle distribution compared to non-sonicated sample. More intense irradiation leads to the formation of smaller particle sizes, and highly dispersed particles were found in intensely irradiated Zr/MCM-41 catalysts [78]. The higher dispersion of Zr with respect to the higher specific surface area determines the accessibility of the reactant into solid surface and, furthermore, gives more stability until the fifth cycle. The adoption of green synthesis of nanoparticles for nanocomposite preparation is also a challenging topic. A homogeneous dispersed ZnO/MCM-41 catalyst was successfully prepared by using orange peel extract [79].

Table 2. Some metal/metal oxide-modified mesoporous silica catalysts and their performance in biodiesel production.

Catalyst	Transesterification Reaction	Remark	Reference
Zirconium-doped MCM-41-supported WO ₃ .	Transesterification of oleic oil	High conversion was maintained at 97% even at in condition of the presence of 5.5 wt% of water, suggesting that water is not adsorbed on the active centers of the catalyst and oleic acid molecules.	[46]
CaO/SBA-15	Transesterification of sunflower oil and castor oil by using methanol	The conversion was 65.7 and 95% for sunflower oil and castor oil, respectively.	[63]
MgO/SBA-15	Transesterification of lauric acid with butanol	Incorporation of Mg into mesoporous silica does not affect the structure. The catalysts were able to promote the esterification of lauric acid with 1-butanol, giving good yields at ambient pressure.	[80]
MgO/ZSM-5	Transesterification of <i>Spirulina</i> oil	Catalyst is reusable until the fifth cycle.	[67]

Table 2. Cont.

Catalyst	Transesterification Reaction	Remark	Reference
MgO/KIT 6	Transesterification of vegetable oil	Reaction conversion of 96%.	[66]
Cs/SBA-15	Transesterification of canola oil	A conversion of 99% was achieved with the pressure of 3 MPa and reaction temperature of 260 °C.	[81]
Ce/MCM-41	Transesterification of sunflower oil	Catalyst shows stability, which is related to the homogeneous distribution of Ce in the nanocomposite.	[76]
Zr/MCM-41	Transesterification of sunflower oil	Catalyst was prepared through ultrasound irradiation. It was found that the frequency of ultrasound influenced the Zr distribution and specific surface area, thus affecting the catalyst stability.	[78]
ZnO/MCM-41	Jatropha oil transesterification	Catalyst was prepared using orange peel extract as a green reductor of ZnO nanoparticles. Catalyst showed high activity (97% conversion).	[79]
TiO ₂ /MCM-48	Palmitic acid photocatalytic transesterification	The prepared material shows photocatalytic activity for the photocatalytic esterification of palmitic acid, and the material is recyclable until the 10th cycle.	[77]
Cr/SiO ₂	Palmitic acid photocatalytic transesterification	The prepared material shows photocatalytic activity for the photocatalytic esterification of palmitic acid under solar irradiation, and the material is recyclable until the 10th cycle.	[82]

Photocatalytic transesterification is another green chemistry approach for biodiesel production, and the utilization of TiO₂ nanoparticles and TiO₂/MCM-48 was successfully recorded [77,83]. In principle, as the photocatalyst is impinged by the UV light, there will be electron excitation from the valence band (VB) into the conductance band (CB), at the same time, generating the same number of photogenerated holes (h⁺) in the VB. The combination of the generated hole with adsorbed methanol as the reactant leads to the formation of free radicals (CH₃O·) and, similarly, with the adsorbed free fatty acids (FFAs), R-COOH generates R-COO·. The collisions between methanol radicals (CH₃O·) and the carbonyl carbons on R-COOH· form intermediates. In a further third step, the dehydration of the intermediate rearrangement produces biodiesel. Technically, vigorous stirring in the process of reactant adsorption and product desorption is conducive to the reaction since it facilitates the transfer rate of reactants and products at the interface and in the liquid phase [77,84,85]. TiO₂ is a well-known photoactive material for this mechanism, as the band gap energy effectively catches the photon source for creating radicals for the mechanism. As a non-photocatalytic mechanism, the study on palmitic oil transesterification expressed that the conversion depends on several factors of the reaction such as the length of the carbon chain of methanol, methanol:oil ratio, and stirring speed. For the various alcohols, the conversion was increased in the following order: butanol < isopropanol < ethanol < methanol [77]. By a different photocatalytic mechanism, Cr/SiO₂ demonstrated photoactivity in transesterification under solar radiation. The prepared Cr/SiO₂ composite photocatalysts expressed strong photo-absorption both in the UV and visible electromagnetic regions (230, 380, 440 nm, and between 500 and 700 nm). The photo-illumination of the photocatalyst caused an electronic reduction of Cr⁶⁺ and Cr³⁺, which generated H⁺, CH₃O·, and R-COOH· radicals in high concentrations at the photocatalyst surface. A further surface mechanism is similar to the mechanism of the TiO₂ photoactive material [82]. In order to enhance the stability of the catalyst for low-

quality oil to biodiesel production, the biofunctionalization of metals/metal oxides with acid/base functional groups was attempted [86]. Bifunctional acid–base catalyst of iron (II)-impregnated double-shelled hollow mesoporous silica (Fe/DS-HMS-NH) and amine-functionalized Ni/Mo-mesoporous silica are the examples for this scheme [87,88]. Based on the studies that have been explored, metal oxide modifications, such as supported metal oxide nanoparticles, can offer better longevity and stability for biodiesel production catalysts. However, metal modification can still be effective, especially if the reaction conditions are mild or cost considerations are critical.

3.3. Mesoporous Silica-Immobilized Lipase

The use of lipase (triacylglycerol acylhydrolase; EC 3.1.1.3) in biodiesel production was reported in 1990 by Mittelbach for the alcoholysis of sunflower oil. The relatively high conversion of nonaqueous alcoholysis in the mild reaction conditions, easy isolation of biodiesel and glycerol of glycerin without further purification, and production without the formation of chemical waste are general attractive features of lipase-catalyzed conversion. As with many other enzymes, the specificity of lipases has great importance in the conversion mechanism. Specifically, 1,3-specific lipases are capable of releasing fatty acids from positions 1 and 3 of a glyceride and hydrolyzing the ester bonds of a plant oil. This generally takes place in two main steps; hydrolysis of the ester bond and esterification with the second substrate.

For industrial applications including biodiesel conversion, microbial-generated lipases are preferred because of their short generation time. Among many different bacterial and fungal sources such as *Candida antarctica*, *Candida rugosa*, *Aspergillus niger*, *Chromobacterium Viscosum*, *Mucor miehei*, and *Rhizopus oryzae*, *Candida rugosa* is the most-used microorganism for lipase production. Although there are several advantages, the use of lipase enzyme comes with problems regarding its expense and instability. Lipase enzymes could lose their activity due to inhibition by the reaction condition and the presence of by-products. The inhibition by insoluble glycerol as a by-product occurs naturally.

Recycling, reusability, and the stability of enzymes in the face of environmental changes are important factors, and as an attempt to achieve these feature, immobilizing lipase into supporting solids is an intelligent strategy. From a technical perspective, lipase immobilization could be conducted to maintain operational stability and catalyst recovery. Immobilized enzymes can be separated from the reaction mixture more easily, and at the same time allow the enzyme to be studied under harsher environmental conditions. Immobilizing lipase is a mid-stream processing strategy along with intensification, optimization, and process design. Many solid supports have also been reported as host of lipase, including polymeric materials, silica-based material, and silica-alumina-based materials. With the consideration of chemical stability and capability of hosting the enzyme effectively, mesoporous silica materials have also been reported. Lipase immobilization can be performed through various mechanisms such as adsorption, cross-linking, encapsulation, entrapment, and hydrophobic interaction [89].

Adsorption is one of the simplest methods, particularly for mesoporous silica support. Generally, enzymes are immobilized after the synthesis of the support through adsorption, to avoid enzyme denaturation caused by harsh conditions or chemical reagents that are detrimental to the enzyme. A simple immobilization method through physical adsorption under a phosphate buffer has been reported [14,90,91]. Controlling surface charge is important, which is explained by the fact that sodium ions act as counterions for reducing the electrical double layer of the silica surface and thereby decreasing the k -potential via the screening effect. Stronger silica–lipase interaction occurs in the presence of a crosslinker such as glutaraldehyde. It was reported that immobilized *Candida Ragusa* lipase (ICRL) on fibrous silica nanoparticles KCC-1 maintained above 81% of the initial activity after 28 days, and 80% of the activity was maintained after 8 repeated cycles [92]. Other crosslinkers include sodium dodecyl sulfate (SDS), ethylene diamine tetra acetate (EDTA), and polyethylene glycol (PEG), even though they generally lower the activity.

The catalyst activity of immobilized enzymes should be through the mechanism of interfacial activation, in which the active site of the lipase in aqueous solution is covered by a flexible region of the enzyme molecule, often called the lid. Interaction with a hydrophobic phase can cause opening of the lid to make the active site accessible. The positioning of lipase onto the support is frequently performed through a hydrophobic interaction between the surface and the lid of lipase. For this, covalent bonding of the linkage to increase the surface hydrophobicity is required. Moderate hydrophobicity/hydrophilicity of the support is the best feature providing lipase activity enhancement. However, too hydrophilic (pure silica) or too hydrophobic (butyl-grafted silica) supports are not appropriate for developing high activity for lipases [24]. As an example, the presence of Triton X-100 in a lipase adsorption system had a detrimental effect, reducing the efficiency more than twofold. The competition for surface adsorption sites is probably the major reason for this [90]. Figure 4 describes the expression of lipase immobilization over adsorption, covalent bonding, and cross-linking methods.

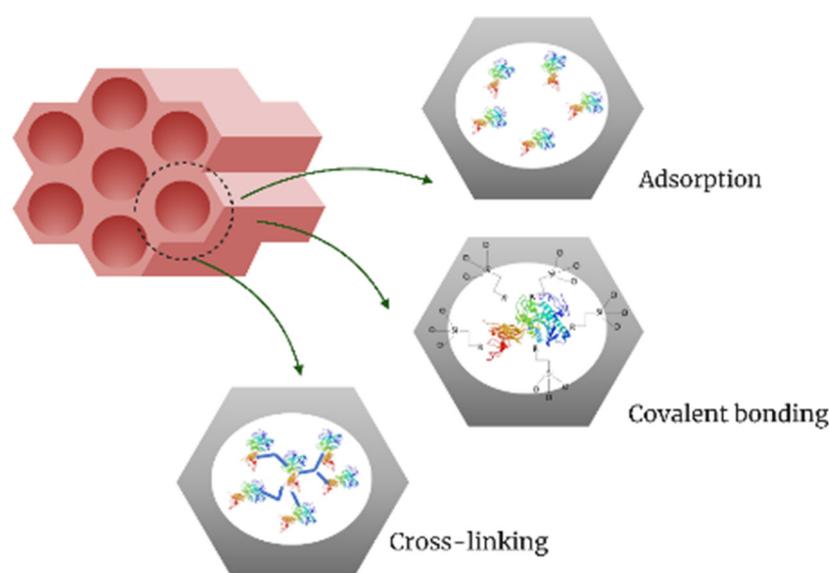


Figure 4. Schematic representation of mesoporous silica lipase immobilized through adsorption, covalent bonding, and cross-linking methods.

Moreover, to provide easy handling and recoverability of the catalytic system, hybrid nanocomposites were created by applying magnetic mesoporous silica materials. The nanocomposites were designed as silica-coated magnetic nanoparticles as a host for lipase. Fe_3O_4 nanoparticles with magnetic properties were the core of the nanocomposite shells to host *Burkholderia* sp. lipase, leading to a biodiesel yield above 90% [93,94]. Greater reusability and thermal stability were achieved through the combination of lipase immobilization onto amine and aldehyde surface-modified mesoporous silica [95]. Superior activity for olive oil transesterification was demonstrated by *Rhizopus oryzae* lipase (ROL) immobilized onto aminopropyl triethylenesilane (AP) and glutaraldehyde (GA) magnetic mesoporous silica. Silica was coated onto Fe_3O_4 before functionalization followed by ROL immobilization, and the material still showed magnetism (~ 20 emu/g). Using the Michaelis–Menten kinetics calculation, the composite shows a reduced K_M parameter, suggesting the substrate's affinity to the enzyme [95].

3.4. Mesoporous Silica-Supported Ionic Liquids

Ionic liquids (ILs) are classified as molten salts with several unique properties and characteristics that can be applied in various fields of application, including catalytic processes. One of the main properties of ILs is their ability to act as phase transfer catalysts (PTCs). This unique property facilitates the transfer of reactants or products between

two immiscible phases, for example, between liquid and gas or solid and liquid phases. The PTC characteristics of ILs also provide several advantages compared to traditional solvents because ILs have good chemical stability, can dissolve various reactants, are thermally stable, and have low volatility. Several studies have shown that ILs containing pyridinium cations, phosphonium, imidazolium, and ammonium act as PTCs for benzoin condensation, nucleophilic substitution, fluorination, and esterification [96,97]. Santiago et al. (2017) reported ILs for enhancing the epoxidation reaction for the selective synthesis of β -O-glycosides [98]. The results showed that the presence of imidazolium ILs could facilitate the transfer migration of reaction between two different phases, aqueous and organic phases. Moreover, Szepiński et al. (2020) investigated surface-active amino acids ILs as PTCs for several different reactions [99].

Their study found that their effectiveness and efficiency as a PTC could be increased quickly and significantly impact their catalytic characteristics, such as changing the cation structure and extending the structural chain. PTCs in different phase systems, for example, in the liquid/liquid phase, facilitate the migration of anionic reagents between phases so that the process drives the reaction to run faster and improves the percentage of yield product. Although ILs have shown exemplary performance in the PTC process, some limitations of ILs as PTCs, especially on a large scale, still need to be overcome, such as low compatibility, difficult recovery and reuse, low stability, or easy degradation [99]. Therefore, ILs can be heterogeneous with solid materials such as mesoporous materials to overcome these limitations. These supported ILs (SILs) provide new findings and opportunities, especially in several reactions in biodiesel production. In addition, SILs allow for more straightforward and efficient catalyst recovery.

Mesoporous material-supported ILs have been widely studied, especially in the conversion and production of biodiesel. These materials provide many advantages, such as dissolving various organic compounds and good stability at high temperatures and pressures. SBA-15 is a mesoporous silica-based material widely developed as a catalyst because it has uniform hexagonal pores with an average diameter of around 15 nm. Besides being cheap, this material also has a narrow pore size distribution and a variety of chemical functional groups, making it easy to modify to increase efficiency. Yuan et al. (2012) reported the heterogeneous catalyst-based basic IL-supported mesoporous SBA-15 for the epoxidation of olefins [100]. The basic ILs, 1-methyl-3-(chloropropyltriethoxysilane) imidazolium chloride (CIL), were attached to the surface of SBA-15 through the surface grafting reaction method. They found that the CIL could be loaded onto mesoporous SBA-15 until 0.39 mmol/g. The CIL-supported SBA-15 showed good catalytic activity for the epoxidation of various olefins compounds, with the highest conversion and epoxide yields until 94% for the cyclooctene compound. This type of catalyst is quite reactive for epoxidation reactions on cyclic olefins and less reactive for open and linear chain olefins. A related study was also reported by Karimi and Vafaezadeh (2012); they investigated acidic IL-supported SBA-15 for solvent-free esterification [101]. Differences in the structure and functionalization of the IL groups assigned to the mesoporous material SBA-15 have been shown to affect the catalyst's phase and mass transfer properties. Acidic hydrophobic [OMIm] [HSO₄] is believed to have efficient mass transfer properties for esterification processes, especially in biodiesel production. Furthermore, this type of IL can also have increased Brønsted acid strength and high reusability because it does not interact with the water produced from the primary reaction process. Figure 5 shows an example of a modified cationic ionic liquid process on mesoporous silica. When cationic ionic liquids are introduced or immobilized onto the surface of mesoporous silica, they can change the properties and functionality of silica materials. The immobilization of cationic ionic liquids onto the surface of silica can increase its catalytic activity, selectivity, stability, and several surface characteristics, as shown in Figure 5. Different types of ILs modified on mesoporous silica can produce various surface areas. Thus, selecting the kind of IL directly affects the characteristics of the resulting mesoporous silica. In addition, the type of modification method used also affects it directly. Various synthesis methods have been studied, but

grafting and impregnation are the primary methods for supporting ILs in mesoporous silica materials [102,103]. Both are general methods that are representative of chemical and physical processes. Impregnation is a method based on physical interaction and is more straightforward; namely, it involves the adsorption of ILs on the surface of mesoporous silica. In contrast, the grafting method uses chemical interactions between ILs and the surface of mesoporous materials. As a result, the grafting method shows better stability but has drawbacks such as complicated and complex preparation methods, requiring a long time, and high costs. These differences in synthesis methods directly affect the morphological properties of the catalyst, such as pore size and surface area. In its application as a catalyst in the production of biodiesel through a variety of different reactions, the specific surface area of the IL-supported mesoporous silica determines the percentage of product produced. However, the pore diameter and the reaction time applied during the process also influence the ratio of products [104].

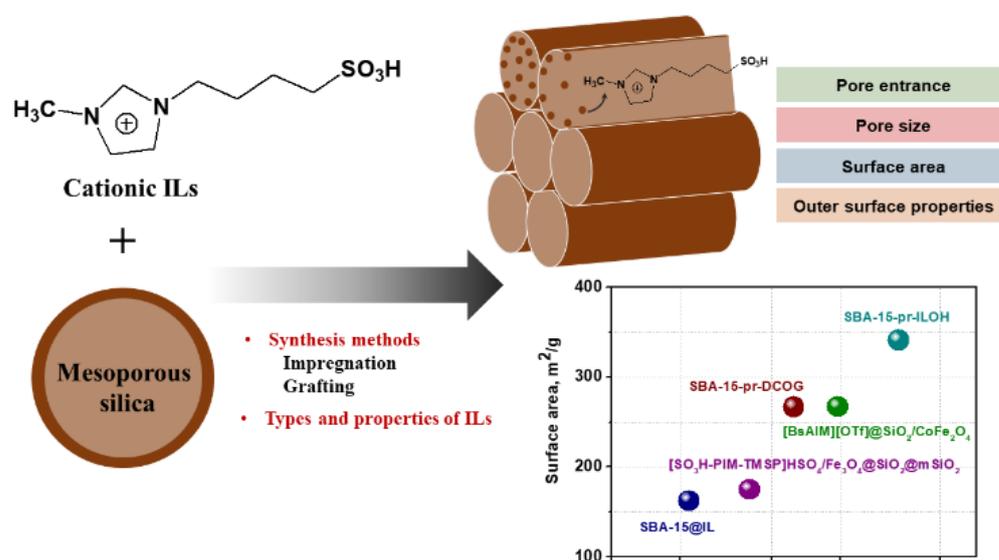


Figure 5. Illustration of heterogeneous IL-supported mesoporous silica synthesis and the surface area properties with different types of IL-supported mesoporous silica.

4. Environmental Impact and Circular Economy Analysis

Using mesoporous silica catalysts in biodiesel production can cause several environmental impacts from the catalyst synthesis process and biodiesel production approaches. The production process of silica catalysts generally involves energy-intensive methods for the synthesis, purification, and activation processes. The energy needed in each process contributes directly to the resulting emissions and environmental impact. However, the amount of energy required depends on several factors, especially the synthesis method chosen and used in the catalyst production. Therefore, to minimize excessive energy consumption during the synthesis process of silica mesopore-based catalysts, several strategies can be applied, such as exploring alternative synthesis pathways and optimizing the conditions for the synthesis reaction. Development and synthesis approaches that are more environmentally friendly and sustainable are one of the most efficient steps in helping to reduce the energy requirements for catalyst production. However, it should be noted that the specific energy requirements may vary depending on the desired characteristics of the catalyst and the scale of production.

In addition to the synthesis method, the raw material used is another factor that influences the environmental impact of using mesoporous silica catalysts. These two factors are closely related to the amount of energy required because they are interconnected with the selection of the synthesis and purification methods. Watanabe and co-workers (2021) reported the synthesis of mesoporous silica from geothermal water [105]. They

concluded that using geothermal water as a source of silica provides an advantage during the synthesis process because the high water temperature can supply sufficient thermal energy for the catalyst synthesis process. Thus, this process will encourage more efficient or lower energy use. El-Nahas et al. (2020) reported a facile synthesis route for zeolite based on waste raw materials such as disposed silica gel as a source of silica and various types of aluminum waste (cans, aluminum foil, scrap wire cables, bottles, etc.) [106]. Studies have proved that using waste as a raw material in synthesizing catalyst materials could reduce production costs by up to 70% compared to commercial raw materials. In addition, selecting appropriate and economical raw materials can reduce the use of chemicals and multi-step procedures in the synthesis process so that production costs are lower than for commercial raw materials.

Furthermore, if we look at the biodiesel production process, the transesterification process has been widely reported to produce several types of by-products, such as solid residue, methanol, biodiesel washing wastewater, and glycerol [107]. However, among the various types of by-products, glycerol is a by-product with a relatively large quantity produced from the catalytic process. Disposal of this waste must be properly managed to prevent environmental pollution and minimize its impact. The conversion and reuse of biodiesel by-products, especially glycerol, has been studied and continues to be developed. For example, glycerol has been widely used to produce high-value biotechnology products such as biosurfactants, 1,3-propanediol, citric acid, and ethanol. This biodiesel production process can lead to an abundant glycerol yield in the future to reduce the price of glycerol sales. Various techniques have been studied to convert glycerol into biotechnology products or more useful renewable energy sources, such as ammoxidation, esterification, acetylation, pyrolysis, gasification, and steam reforming [108].

Therefore, the application and circular economy approach for the synthesis of mesoporous silica for biodiesel production can be viewed in terms of several essential aspects, namely: (1) selection of waste raw materials that are rich in silica sources such as industrial by-products (fly ash), agricultural residues (dregs sugarcane, rice husk), or household post-consumer waste. (2) Selection of resources such as developing efficient synthesis methods with high purity and low energy use. Optimizing the synthesis process to minimize energy consumption, waste generation, and the use of hazardous chemicals can reduce the resulting environmental impact. (3) Emphasis on recycling and reuse of catalyst materials. Developing catalyst materials that are easy to separate and purify is a challenging area of study for the present and the future. Reusing catalyst materials can reduce waste generation and promote a circular approach. (4) Cultivating collaboration between waste feedstock suppliers, catalyst producers, and biodiesel producers to build closed-loop systems and sustainable production is an essential step in adopting a circular economy approach in the future.

Based on the mapping and bibliometric analysis results, as shown in Figure 6, converting waste biomass into biodiesel and bioethanol is still an exciting topic and supports the renewable energy transition policy. The development of alternative synthesis methods that are more environmentally friendly is still a topic that is continuously being studied to reduce the environmental impact of high energy consumption. Servicing raw materials and their availability is an essential factor in developing a sustainable and abundant system for future biodiesel and bioethanol production. Currently, fast pyrolysis involving enzymatic reactions and microorganisms as the main raw material is considered to have the potential to be developed for the production of bioenergy [109].

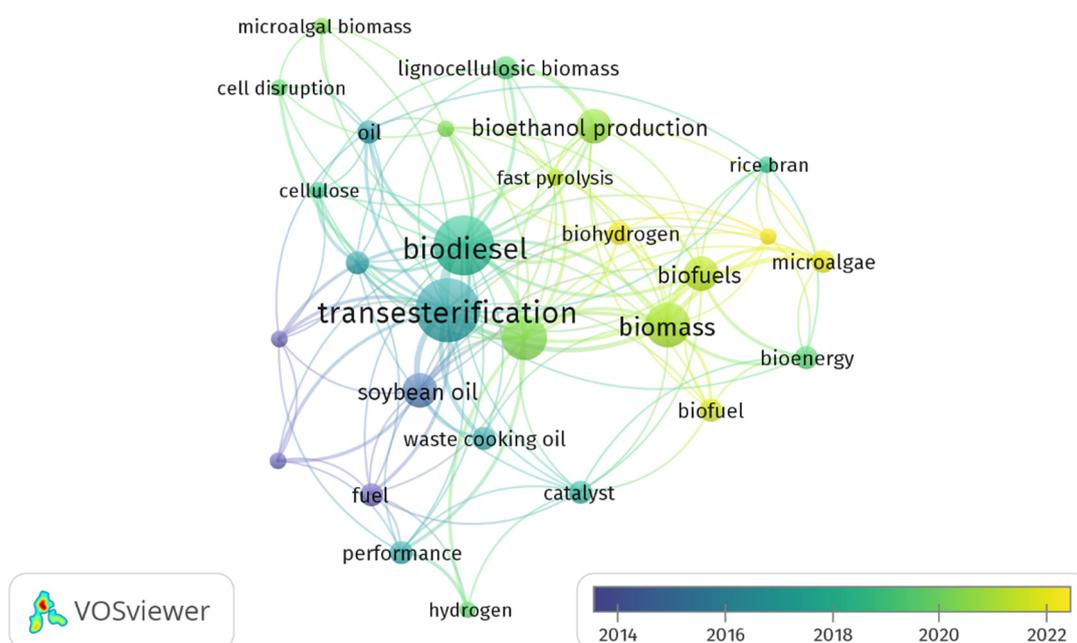


Figure 6. Bibliometric analysis for biodiesel production using mesoporous catalysts (data source: Web of Science, webofscience.com, accessed on 6 June 2023).

5. Conclusions and Outlook

Various catalysts and methods have been proposed for biodiesel production to achieve the optimized conditions and a total low-cost process. Considering the green technology and green chemistry perspective, heterogeneous catalyzed reactions are known as a promising method. Processes with low energy consumption and reusable catalysts are highlighted to fit with the requirements. The present study revealed that the physical and chemical characteristics of the catalyst (such as basicity and acidity) play a pivotal role in biodiesel production. Mesoporous silica materials have been shown to be feasible heterogeneous catalyst supports due to their high specific surface area and tunable properties. Varied surface functionalization methods of mesoporous silica surfaces have been reported with specific features in order to meet the prerequisites of industrial applications. Some issues that can be noted for development include the intensive design of the nanocomposite by applying nanotechnology perspectives, the development of intensified methods, magnetically separable catalysts, ionic liquid modified materials, and the photocatalytic conversion of biodiesel. Immobilized biocatalysts with ultra-selectivity in non-solvent reaction using mesoporous silica are still a promising and relevant scheme of material development. Nevertheless, some nanomaterials from mesoporous silica are still too expensive to be commercialized and to be used for biodiesel production. Silica precursors and other chemicals need to be replaced with feasible materials, and for this issue, some explorations into biogenic silica resources need to be looked at. Sustainable sources of silica such as rice husk, wheat straw, salacca peel waste, and bamboo leaves have been reported to have potential for functionalized silica [110–114]. As the design of catalyst preparation could be inclusively combined with the agricultural industrial cycle, the concept of circular economy to provide biodiesel as a renewable energy resource can be more intensified. It is believed that several newly introduced functionalizations of mesoporous silica along with the intensification of biodiesel production help in producing eco-friendly and economically viable biodiesel. Developing innovative process intensification techniques, such as microreactors, continuous flow systems, or advanced reactor designs that can facilitate increased efficiency and productivity of biodiesel production using mesoporous silica catalysts, still needs further study. In addition, the synthesis of mesoporous silica for biodiesel production at the industrial level is also of interest to consider. Conducting a comprehensive life cycle assessment (LCA) to evaluate the environmental impact of mesoporous silica catalysts on biodiesel

production is essential. Overall, future research should aim to advance the understanding of mesoporous silica catalysts in biodiesel production, addressing challenges related to stability, catalyst design, feedstock flexibility, and process optimization, seeking sustainable and efficient development.

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