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Review Article

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Heterogeneous catalysis: an alternative approach for energy and environment

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Abstract: The uncontrolled increase in population and human activities has led to a significant rise in the demand for energy resources. The excessive use of limited fuel sources, unplanned deforestation, and greenhouse gas emissions have necessitated the search for and development of alternative, sustainable energy resources that cause minimal or no harm to the environment. The introduction of green and eco-friendly technologies offers a potential solution to address the growing demand in fields such as petroleum and hydrogen production, with the ultimate goal of promoting environmental sustainability. This review article highlights recent innovations in the field of heterogeneous catalysis, focusing on the development of various catalytic materials and processes, as well as their future prospects for both industrial and academic advancements. A brief discussion is presented on the efficient performance of solid acid and base catalysts, metal-organic frameworks (MOFs), electrocatalysts, and photocatalysts. The discussed catalytic systems have been explored for their potential applications, including biodiesel and hydrogen production as alternative energy sources, as well as CO_2 reduction and the degradation of toxic dyes and organic pollutants for environmental remediation. Overall, the significance of heterogeneous catalysts has been explored, emphasizing their critical role in driving industrial progress and economic growth.

Keywords: heterogeneous catalysis; solid acid catalyst; solid base catalyst; photocatalysis; environmental remediation

1 Introduction

Catalysis is a fundamental element of many chemical processes and hence it is a main strength of all chemical industries.[1] It is proven and now a day there is a growing concern about the catalysts that are environmentally friendly and safer technologies for the better industrial productions. Not less than 15 Nobel prizes have been awarded for studies on catalysis and many chemists around the world are repeatedly advancing the catalysts they have, and are motivated to discover new ones.

All the catalytic process can be applied either homogeneous or heterogeneous catalysis. Heterogeneous catalysis is a process in which catalyst being used is in a different phase than the reactants, i.e. the catalysis is usually in a solid phase and the reactant is in a liquid or in gaseous phase. As a part of catalysis, heterogeneous catalysis has prior importance in many areas of the chemical research for energy and environmental applications.[2,3] Although, there are many advantages of homogeneous catalysis which is pH dependent and can function with wide pH range.[3] Further, overall, most of (>80 %) chemical and bio-catalytic processes well established with heterogeneous catalysis and thus it is much successive catalytic process of vibrant branch of chemistry as well as pharmaceutical world. Figures 1–3 emphasizing the importance of the catalytic process and among all the process, how heterogeneous catalysis being a large part of chemistry itself can be found here.[4,5]

The beginning era of heterogeneous catalysis, academic research and industrial processes were focusing on production of bulk chemicals and refining the oil as fuel on large scale requirement and it has been expanded rapidly in the recent decades.[6,7] Heterogeneous Catalysis is now become a key factor for many industries for the conversion of petroleum and natural gas into cleaner and efficient fuels, but now there is a demand for the production of alternative fuels such as hydrogen and biofuels.[6–8] Heterogeneous catalysis is still in use for the selective synthesis of special intermediates or products and fine chemicals in bulk production. Now a day it is possible to find the alternative route for the energy and environmental issues due to major advances in the design and development of catalyst at the molecular level.

In continuation, there are many efforts in progress to unlock energy sources that are much more difficult to use than fossil fuels, but are “greener”, where heterogeneous

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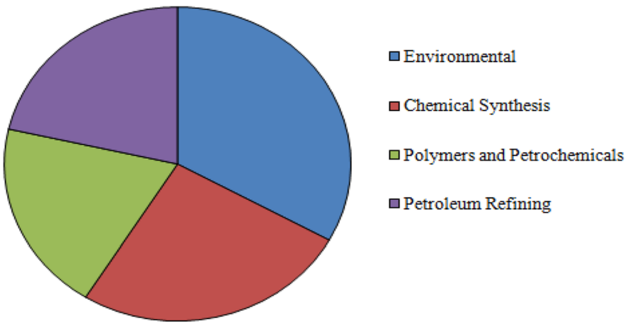

Figure 1: Global catalyst market share 2018 (%) by applications [4]

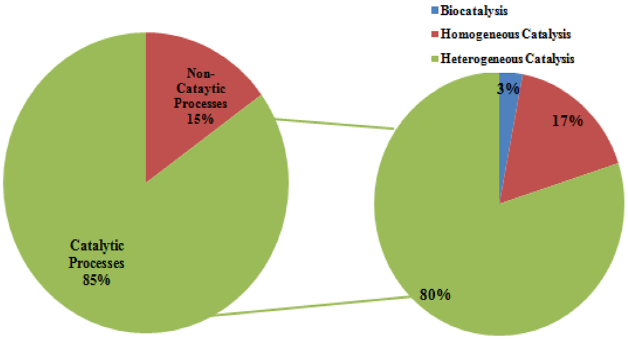

Figure 2: Involvement of catalytic and non-catalytic process to the chemical industries [5]

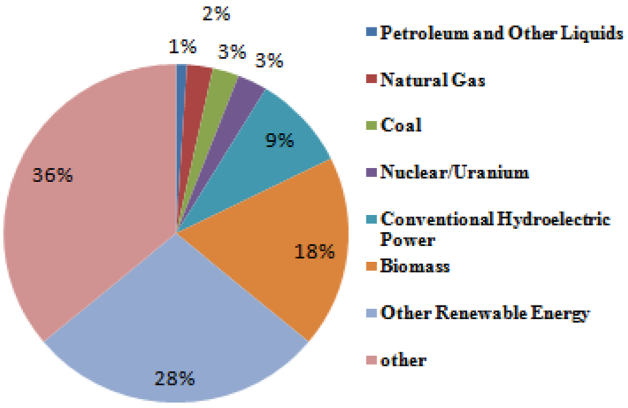

Figure 3: Involvement of heterogeneous catalytic systems to various fields [5]

photocatalysis could make it economically feasible to produce hydrogen fuel from water splitting and leads to find novel methods to produce efficient energy sources from the raw resources such as CO_2,[8] biomass [9] etc. Green technologies have included heterogeneous catalysis as being advantageous for regeneration and reusability, production of no waste or very less amount of waste, easy set up process with lower cost, high thermal and chemical stabilities and good selectivity of final product. Indeed, heterogeneous catalysis is being used for the environmental remediation for water, air and soil by applying an environmentally benign approach.

The conceptual platform for the practicable uses of catalytic systems can be defined by energy and mass dimensions. It consists of processes and materials being used with mass inputs in terms of raw materials to be converted into added-value ones directly or indirectly equal to the energy resources with or without emissions to be treated.[10,11] In this context, the consumed energy can be considered an input for endothermic reactions, while the energy generated serves as an output for exothermic reactions. Light, heat and electrons are often considered specific resources that promote catalytic systems by adding energy, leading to processes such as photocatalysis or photoelectrocatalysis.[10,12,13]

The types of catalytic systems can be identified based on the structure and nature of the catalytic materials, which impart their catalytic functionality. Table 1,[14–31] and Figure 4 illustrate the most commonly used catalytic processes and materials.

There are also some drawbacks of heterogeneous catalysis such as it requires higher temperature and pressure for the reaction to occur, thus it requires higher energy consumption and therefore utility and energy related costs are very high.[2] To develop and design a highly efficient and environmentally-friendly catalytic materials and

Table 1: Types of catalytic processes commonly used.

No.	Catalytic processes	Ref.
A	**Oxidation**	
1	Advanced oxidation process	14–17
	– To eliminate the degradability of organic pollutants like dyes	
	– Decomposition of water into hydrogen and oxygen	
	– Oxygen evolution reactions (OERs)	
2	Oxidation of SO*x*, NO*x* and CO*x*	18
	Oxidation of carbon monoxide to carbon dioxide (CO_2)	19
3	Oxidation of alkanes, alkenes and aromatics	20
4	Oxidation of alcohol (methanol to CO_2)	21
B	**Hydrogenation**	
5	Hydrogenation process of vegetable oils	22
6	Hydrogenation of alkenes and aromatics	23
7	Formation of ammonia	24
8	Hydrogenation process of CO_2	25
9	Hydrogenation or hydrocracking of plastic and rubber waste	26
C	**Dehydrogenation**	
10	Dehydrogenation for H_2 production	27
D	**Reforming**	
11	Catalytic dry reforming of methane	28
12	Catalytic reforming of biofuels	29
13	Catalytic reforming of oxygenates	30
14	Dry reforming processes for hydrogen production	31

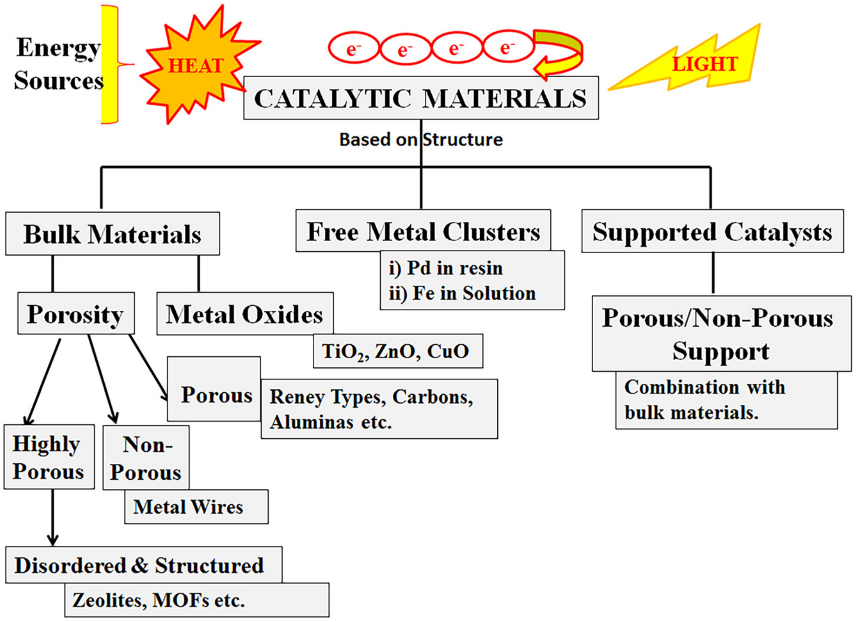

Figure 4: The types of catalytic systems based on structure.

systems are very effective approaches to generate novel energy sources and remediation of contaminated soil, air and wastewater.[6,7b] Thus, the bridging connection between a material structure and chemistry with efficient performance of heterogeneous catalyst would provide rational informations for catalyst design and addressing the challenges in promising use in the research area of energy resources.

The current review article shows recent development and progress in heterogeneous catalysis for energy and environmental applications. Heterogeneous catalysis consists of many subclasses depending on nature and structure of the catalyst used in solid phase such as solid acid catalyst, solid base catalyst and nano catalyst.

2 Energy applications

2.1 Biodiesel production

Currently, the use and storage of fuel energy for economic development and finding of an alternative fuel sources are in prior demand due to the ever-increasing world population. It is now an urgent worldwide issue to implement the possible all the efforts for the sustainable automotive fuels.[7] Since, last few decades, the biodiesel production has been promoted on the large scale as a safe and novel technology. Biodiesel belongs to the class of renewable and sustainable fuel source receiving more attention as rapidly growing field with high potential rather than other energy sources and evidently beneficial for a long-term investment.[32–34]

Processes for biodiesel production can be classified as catalytically, chemically (base or acid catalysis), biologically (enzyme catalysis) and non-catalytic processes. Chemically, biodiesel (alkyl-ester derivatives) is usually produced by chemical catalytic transesterification of refined vegetable oils/waste cooking oils (long chain fatty acids) or animal fats. The chemical catalysts used earlier are strong acidic (HCl, H_2SO_4, HF, *p*-toluenesulfonic acid) or basic solutions (NaOH, CH_3ONa and KOH).[7b]

Now days, a “green” approach for biodiesel production has been adopted the use of sustainable solid acid catalysts as replacements for such liquid acid catalysts so that the use of harmful/corrosive substances and unwanted formation of toxic wastes could be avoided. With remarkable developments and fruitful researches reported in the past few years for the industrial production, heterogeneous catalysis is growing up in the market for the biodiesel production.[7b,33a] Heterogeneous catalytic transesterification is a process where the catalysts remain in different phase to that of the reactants and provides easier separation of biodiesel from glycerol.[35–37] The catalytic conversion of oil into biodiesel is slowly but the resulting biodiesel could be possible in an economical way.[38,39] Firstly, surface morphology characteristics, having large pore size to minimize diffusion problems is an ideal characteristic of a solid catalyst as being a part of heterogeneous catalysis. Another one, is deactivation, mainly achieved because of availability more active catalytic sites, high catalytic stability versus leaching and the probability to tune the hydrophobicity of the surface with the repulsion of highly polar compounds.[40] From the literature, solid base catalysts such as base zeolites, alkali earth metal oxides, hydrotalcites (or layered double hydroxides), alumina loaded with various compounds and mixed oxide have been quite successful with high conversion and yield of biodiesel obtained.[33b]

2.1.1 Solid acid catalyst (SAC)

SAC can be defined on the basis of nature and number of present active acid sites (Brønsted or Lewis acidity), arability of the acid sites and morphology of the support. Therefore, the acid catalysts could be used directly for biodiesel formation from low-grade, highly-acidic and water-containing oils. Thus, solid acid catalysis is now well established as benign alternatives to the unrecyclable-homogeneous acid catalysts and succeeds in the petrochemical industries. Many more benefits avail to this class of catalysts such as, (i) the catalysts could be modified and tunable, selective and easy regenerate and reuse, (ii) minimize product contamination through easy separation from target product, (iii) elimination of washing step particular for biodiesel production, (iv) replaced use of corrosive liquid acids and thus corrosion issue could be minimized, (v) could be employed in continuous flow process, (vi) minimum catalyst deactivation, (vii) catalyst could be rapidly prepared through economically and environmentally affordable process.[3] The surface morphology of the solid catalyst plays a key role for better catalytic performance through selective adsorption of reactant molecules and converts into the desired product. However, many more finding has to search out to connect and fill the knowledge gap between the fundamental concept of reaction pathway and the mechanisms of reactants on the solid catalysts.

They are mainly used for important acid catalyzed organic transformations such as Friedel-Craft alkylation/acylation, esterification/transesterification, acetal/ketal formation etc.[7b] Literature report highlighting the extensive use of solid acid catalysts for biodiesel production through esterification or transesterification processes. For example, the mechanism of the acid catalyzed transesterification reaction of triglycerides is well understood.[6,41,42] Still there are some challenges facing for biodiesel production such as to increase rate of reaction and to reduce unwanted side reaction. Thus, these challenges lead to develop a novel, efficient and stable catalytic system and more efforts for reduction in cost of preparation the catalyst and sequentially reduced biodiesel production costs. There is lots of research work in progress to overcome the said challenges through potential application of various solid acid catalysts for biodiesel production.

The ideal characteristics of a solid acid catalyst are strong Brønsted and/or Lewis acid properties, unique porosity or textural properties and a hydrophobic surface. Till date, the catalytic potential of solid acids have been reported for the biodiesel production such as acidic inorganic ion exchangers, acidic clays, metal oxides, mixed metal oxides, H-form zeolites, heteropolyacids (HPAs), modified silica, acidic ionic liquids, hybrid organo-inorganic materials and carbon based materials.

The Brønsted acid sites are highly polarized hydroxyl groups at the surface of the catalyst that serve as the H^+-donor, while the Lewis acid sites are coordinatively unsaturated cationic sites, which leave the exposed M^+ ion to interact with guest molecules and act as the acceptor of the electron-pair. With respect to base catalysts, biodiesel production processes based on the use of solid acid catalysts are effective alternatives to the conventional processes because of their easy workup and the simultaneous promotion of esterification and transesterification reactions without soap formation.

Zeolites and zeolite type materials: Zeolites are naturally abundant three dimensional frameworks with crystalline structures of aluminosilicates interlinked by oxygen atoms. They contain Al, Si and O in their framework, and cations, water and/or other molecules within their pores.[34] They are well established and robust materials because of having molecular porous structure with channel of uniform sizes gives materials to be ion exchange characteristic. The catalytic activity depends on replacement of Si^{4+} by Al^{3+} with crystalline SiO_2 framework which generates negative charges in the catalyst framework and thus improves catalytic activity. Interestingly, the adsorption ability could be modified through synthesis methods as expected due to the strong electric field created by the loosely held cations within the catalyst framework. Thus, desired catalytic performance in term of good activity and selectivity could be obtained as it has ability to introduce active sites within the pores and channels.[3]

Zeolite can accommodate number of cations such as Na^+, K^+, Ca^{2+}, Mg^{2+} and many more from which it has its basic nature. H-ZSM-5, H-MOR, H-BETA and H-USY are H^+ ion exchanged acid form zeolites found to be not much catalytic active for esterification or transesterification reactions of biodiesel production due to internal diffusion limitations of the bulky reactant molecules into the micro-pores of zeolites.[3] Zeolites Y are weak solid acid catalyst while Zeolites β are three-dimensional structure of 12-membered ring channels with high silica content having both Lewis and Brønsted-acid sites. Lewis-acid sites are mainly present in the micro-porous walls. Zeolite β does not exhibit high activity in transesterification, but it could be used for selective removal of FFAs in waste oil. Silicoaluminophosphates, the recently developed Zeolite types materials foe examples, $SAPO_4$, $ALPO_4$, $MeAPSO_4$ and $MeAPO_4$ could be synthesized with coordinated Al, Si, P, transition metals and other elements.[3]

The catalytic activity of the protonated form of H–Y zeolite (Faujasite with high Si/Al ratio) has been investigated as solid acid catalyst for esterification of oleic acid with methanol.[43] At optimized conditions, methyl esters production yield reaches up to ~95 % and the used catalyst could be regenerated easily and reused for the same. Septiani et al. [44] have prepared Zeolite ZSM-5 and studied its catalytic activity for the transesterification of vegetable oil for biodiesel production. The results of the catalytic reaction show a maximum biodiesel yield of ~92 % at the optimized reaction time and temperature. Zeolite and zeolite-based heterogeneous catalysts [43–69] for biodiesel production have been summarized in Table 2.

Metal oxides: Metal oxides are materials of typical characteristics such as thermal and mechanical stability, high specific surface area, and large pore size and pore volume. Thus, they are extensively being used as catalyst supports for catalytic purpose.

Table 2: Zeolites and zeolite-based heterogeneous catalysts for biodiesel production using esterification or transesterification reactions.

Sr. No.	Catalysts	Esterification/transesterification reactions molar ratio of oil: alcohol	Ref.
1	H–Y(80) zeolite (faujasite with high Si/Al ratio)	Esterification of soybean oil Oil: methanol = 1:3, 1:6 and 1:9	43
2	Zeolite ZSM-5 prepared from rice husk ash	Transesterification of vegetable oil Oil: methanol = 1:3	44
3	H-zeolite	Transesterification of vegetable oil Oil: methanol = 19.4:1	45
4	Y-type zeolites with Al_2O_3 and Na_2O	Transesterification sunflower and waste oil Oil: methanol = 12:1 to 48:1	46
5	Faujasite (FAU)-type zeolite prepared using Irish shale rock	Esterification of vegetable oil Oleic acid: ethanol = 4:1–15:1 by mass	47
6	KOH/zeolite prepared by impregnation in KOH	Transesterification of waste sunflower oil Oil: methanol = 1:1.51	48
7	KOH/Bentonite prepared by impregnation method	Transesterification of refined soybean oil Oil: methanol = 6:1 –14:1	49
8	Y-type zeolites, with different Al_2O_3 and Na_2O percentage	Transesterification of vegetable oil Oleic acid: methanol = 6:1	50
9	ZSM-5 and beta hierarchical zeolites	Transesterification of algae oil Oil: methanol = 100:1	51
10	Alkali loaded low-Al zeolite beta	Transesterification of triolein Oil: methanol = 1:15 (w/w)	52
11	Zeolite linde type a (LTA, dehydrate form)	Transesterification of triolein (methanol in excess)	53
12	KOH/Zeolite prepared by impregnation method	Transesterification of triglyceride with excess methanol	54
13	Natural zeolite bayah banten with KOH impregnation method	Transesterification using vegetable oil *Jatropha* oil: methanol = 1:1	55
14	Zeolite based catalysts prepared from fine powder and kaolinite using pelletization method	Simultaneous transesterification and esterification of waste cooking oil Oil: methanol = 1:5	56
15	Natural zeolite with potassium impregnation	Transesterification of rice bran oil Oil: methanol = 1:6 to 1:12	57
16	Zirconia supported on Indonesia natural zeolite	Esterification of palm oil sludge Oil: methanol = 1:4	58
17	KOH/NaY zeolite prepared by the impregnation method	Transesterification of palm oil Oil: methanol = 1:15	59
18	KOH/Al_2O_3 with varying KOH loadings prepared by the impregnation of the Al_2O_3 support	Transesterification of vegetable oil Oleic acid: methanol = 1:15	60
19	NaX zeolite impregnated with mixture of CaO nanoparticles/ethanol	Transesterification sunflower Oil: methanol = 1:6	61
20	Sodic potassic clinoptilolite and sodic potassic calcic clinoptilolite zeolites	Transesterification of waste cooking oil Oil: methanol = 68–27 (vol%)	62
21	Lanthanum-natural zeolite (La/Zeolite)	Transesterification crude palm oil Oil: methanol = 1:9	63
22	ZnO/Zeolite, PbO/Zeolite	Esterification of *Jatropha* oil Oil: methanol = 1:6	64
23	Zeolite X and a from flyash using hydrothermal treatment	Transesterification of refined mustard oil Oil: methanol = 1:6	65
24	Zeolite MCM-22 and zeolite beta	Transesterification of triolein in excess methanol	66
25	Zeolites loaded with CH_3COOK	Transesterification of *Jatropha curcas* Oil: methanol = 1:10	67
26	HZSM-5 and HZSM-5 impregnated with sulfated lanthanum oxide (SO_4^{2-}/La_2O_3)	Esterification of oleic acid Acid: methanol = 1:5, 1:10 and 1:20	68
27	Commercial H–Y and ZSM-5 zeolite	Esterification of palmitic acid Acid: methanol = 1:2	69

The typical superacids such as SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2, SO_4^{2-}/Ta_2O_5, SO_4^{2-}/Nb_2O_5 etc.[7b] They possess potential economic and green benefits for a number of hydrocarbon reactions under mild reaction condition and thus, interest has been generated to use of such materials for trans-esterification and esterification reactions to produce biodiesel.[70] Herein, an interesting factor about the metal oxides (ZrO_2, TiO_2, Ta_2O_5, Nb_2O_5), they possess the both Brønsted and Lewis acidity that can be improved by modifying its surface by sulfate groups which makes materials to be promising catalyst to promote protonation in the esterification process.[71] Castro et al. [72] have studied heterogeneous solid acid catalysis for esterification and transesterification processes for biodiesel production as renewable fuels to meet the future societal requirements. The authors have prepared sulfated niobium oxide (Nb_2O_5/SO_4) impregnation method and used as solid acid catalyst for biodiesel production from macaw palm oil via high free fatty acid content transesterification with ethanol. As results, the catalyst Nb_2O_5/SO_4, exhibits excellent catalytic activity towards biodiesel production (about ~99 % ester content). The spent catalyst could be reused up to five consecutive catalytic cycles which shows excellent yield of the desired products and the reducing of the yield after fifth catalytic cycle could be due to the handling/physical loss of the catalyst during recycles and regeneration.[72] Sulfated zinc oxides SO_4^{2-}-ZnO and SO_4^{2-}/ZnO have been synthesized by co-precipitation and impregnation respectively and characterized as active solid acid catalyst.[73] The prepared catalysts have been used for trans-esterification of soybean oil with methanol to compare their performance for biodiesel production. As results at optimized reaction conditions, SO_4^{2}–ZnO prepared by co-precipitation method exhibit highest catalytic activity and obtained FAME yields of ~80 %.

Sulfonic ion exchange resins such as Amberlyst-15, –16, –35, –36 and –131, [74,75] Nafion resins [76–80] as SAC-13 and NR50 and EBD-100, -200 and –300,[81] were commonly used heterogeneous catalysts and found to be effective in liquid phase esterification and trans-esterification reactions. The protons bonded to the sulfonic groups are the responsible for the strong acidic active sites which are available on the cross-linked polymeric matrix of these ion exchange resins. The catalytic activity more depend on their surface properties which in turn effective populations of the acidic active sites for the trans-esterification and esterification reactions.

Mesoporous silica (SBA-15) supported ZnO/SBA-15 and MgO/SBA-15 have been prepared and characterized for solid acid catalytic activity. The results show that catalysts exhibit good catalytic activity and promote the esterification of lauric acid with 1-butanol to produce biodiesel (~81 % yield of butyl ester) under atmospheric pressure and reflux conditions.[82] Tesser et al. have prepared Niobia supported catalyst by impregnation of silica pallets with loading of Nb and characterized for catalytic characteristics. The prepared solid acid catalyst has been used in both transesterification (free acid methyl ester conversion) and esterification (free fatty acid conversion) reactions of triglycerides for biodiesel production. The study, Nb supported on silica found to be much active in both the mentioned reactions with no loss of catalytic activity in the continuous run of 100 h but slow leaching of Nb observed which could be reduced the catalytic potential.[83] Xie et al. prepared lithium doped zinc oxide (Li/ZnO) using impregnation method followed by calcination at different temperatures and evaluated its catalytic activity for transesterification of soybean oil with methanol at optimized reaction conditions.[84] As results, Li/ZnO exhibits good catalytic activities towards soybean conversion to ester as obtained ~96 % yields. The catalytic sites are in basic nature which is due to formation of Li_2O from thermal decomposition of $LiNO_3$ at higher calcination temperatures. The authors also have prepared CaO–MoO_3-SBA-15 by incipient impregnation method with different calcination temperatures and tested for the similar transesterification reaction of soybean oil with methanol for biodiesel production.[85] The prepared solid catalysts, a catalyst with loading of 40 % and calcined at 550 °C shows highest catalytic activity (~83 % yield of oil conversion) at the optimized the reaction conditions. The catalyst could be easily revered and reused without loss of its potential catalytic activity.[85] Viswanathan et al. [86] prepared sulfated Fe_2O_3–TiO_2 from ilmenite and calcined for different temperatures. The prepared catalyst examined for its acidic active sites and used for conversion of vegetable oil to biodiesel via trans-esterification reaction with methanol. As results, the catalyst calcined below 500 °C shows higher conversion of vegetable oil with remarkable yield of biodiesel which is attributed to the high affinity of hydroxyl groups of methanol on Fe_2O_3–TiO_2. The removal of sulfate groups has been observed during calcination on above 500 °C could reduce % yield of biodiesel production.[86]

Mixture of strontium and nickel oxide has been synthesized by coprecipitation method followed by different calcination temperatures and characterized for catalyst properties.[87] The prepared catalysts have been used as heterogeneous catalysts for the transesterification of macaw palm oil with methanol for biodiesel production. The catalyst with the calcination temperature of 1,100 °C has highest catalytic activity as achieved ~97 % conversion at the optimized reaction conditions as well as recycling studies also favoring the good % yield for the five catalytic runs.[87]

Ong et al. [88] have studied catalytic activity of the carbon supported CuO catalyst in which the copper nanoparticles have been synthesized by sol-gel method and the nanoparticles impregnated into the pore network of the carbon supported. The prepared catalysts used in esterification of free fatty acid in the rubber seed oil and ~95 % of the free fatty acid conversion was obtained at the optimized reaction conditions. The catalytic performance is comparable to the liquid acid H_2SO_4 as well as compared with other heterogeneous catalysts, the carbon supported-CuO could performed at lower temperature. The reusability study also shows about easy recovery and separation of the catalyst after process completion however it found with lower activity in the use of first catalytic cycle. Zhang et al. [89] have prepared sulfonic/carboxylic dual-acid catalyst based on sulfur-rich graphene oxide (GO-S) as cost effective SAC used for the esterification of the oleic acid with methanol to produce methyl-ester as biodiesel. The results show, GO-S exhibits good catalytic performance in term of activity and reusability which has high TON factor compared to other carbon based SACs. Having a two-dimensional layered structure and the strong synergetic effect between–SO_3H and–COOH groups on the graphene nano-sheets, are the key factors for the catalytic activity of GO-S.[89] The study reveals the promising use of the GO-S in the esterification of the waste fatty acids to convert into the valuable biofuels.

2.1.2 Solid base catalysts

Metal oxides: Recently, alumina has been exhibited as a good support for catalytic material in catalytic process due to having good characteristics such as thermal and mechanical stabilities, high surface area, large pore size and pore volume.[90] Anisuzaman et al. have prepared CaO-supported basic alumina catalyst by impregnation method followed by calcination temperatures and characterized for their catalytic properties.[90]

Alkali metal oxides (CaO, MgO and BaO) doped silica (SiO_2) has been synthesized using sol-gel method followed by different calcination temperatures and used as base catalysts for the biodiesel production.[91] The catalytic transesterification reaction of corn oil with methanol shows that the catalyst CaO/SiO_2 exhibits highest biodiesel production compared to other catalysts with the purity and yield of ~97 % and ~82 % respectively.[91] Ismail et al. have synthesized calcium oxide (CaO) from mud clam shell and used as potential heterogeneous catalyst for the biodiesel production.[92] The results of the catalytic transesterification reaction of castor oil with methanol show a good efficiency of CaO catalyst with the obtained ~96 % yield of biodiesel formation using the optimum reaction conditions as well as the CaO catalyst from mud clam shell could be recycled and reused up to five catalytic runs.[92] Thitsartarn et al. also have reported calcium doped cerium-incorporated SBA-15 (Ca/CeS) synthesized by direct synthesis of Ca-incorporated-SBA-15 followed by impregnation of CaO.[93] The catalytic studies, the Ca/CeS shows excellent catalytic performance for biodiesel production trough catalytic transesterification of palm oil with methanol and also the highest catalytic activity found amongst the other supported catalyst such as CaO/CeO_2 and CaO/CeO_2-SBA-15. As being heterogeneous catalysis, negligible leaching of elements was observed due to strong interaction between CaO and CeS support. Furthermore, beneficially the catalyst could be reused for 15 catalytic runs with insignificant decrease in catalytic activity which reveals the very good efficiency of the catalyst for the biodiesel production.[93] Heterogeneous strontium oxide/calcium oxide (SrO–CaO) mixed metal oxides catalyst has been used in the ultrasonic-assisted transesterification of *Jatropha* oil into biodiesel. The catalyst characterization and the catalytic studies show that the prepared catalyst exhibits high efficiency for the conversion of *Jatropha* oil into biofuels.[94]

Biodiesel production from non-edible *Jatropha* oil has been reported using acid-base bi-functionalized CaO–La_2O_3 heterogeneous catalyst.[95] The catalyst comprising CaO and La_2O_3 mixed metal oxides with different Ca/La ratios have been prepared by using co-precipitation method. As results, the highest biodiesel yield of ~98 % has been achieved and binary catalyst system found to be more stable which was supported by recycling and reusability of the catalyst even after four catalytic cycles. The observed very good catalytic activity in the mixed metal-metal oxide is due to well dispersion of CaO on composite surface which enhance both surface acidic and basic sites as compared to that of bulk CaO and La_2O_3 metal oxide.[95] Wang et al. [96] have reported a series of acid-base bi-functional metal-boron catalysts prepared by sol-gel method followed by calcination temperatures and characterized by spectral and surface characteristics. Amongst the prepared catalysts, the Ca-Boron (700 °C) catalyst shows highest catalytic performance for the production of biodiesel with high acid value (yield of ~98 %) through transesterification reaction of non-edible oil (*Jatropha*) with methanol using optimized reaction conditions. The catalyst exhibits a good stability and reusability which makes it promising acid-base bi-functional catalytic material for the biodiesel production.[96]

Lee et al. [97] have studied the catalytic activity of mixed metal oxides (MMOs) (CaO–MgO, CaO–ZnO, CaO–La_2O_3 and MgO–ZnO) synthesized by co-precipitation method followed by calcination at different temperatures. MMOs contained high basicity and strong basic strength compared to single metal oxide which shows excellent catalytic performance in the transesterification process. As results of the studied catalytic reactions, the Ca-based MMOs catalysts exhibit highest catalytic activity in term of ~90 % yields of biodiesel production and reusability with low metal leaching. Amongst three Ca-based MMOs, CaO–ZnO has comparative high conversion rate with ~94 % yield of biodiesel and could be used for four catalytic cycles with negligible loss of activity.[97] Yigezu et al. [98] have studied catalytic activity of metal oxides such as Co_3O_4, KOH, MoO_3, NiO, V_2O_5 and ZnO for catalytic conversion of oil into organic liquid products. As results, the catalysts are found to be suitable and active solid catalysts for the catalytic cracking of vegetable oil for bio-fuel production.[98]

The review chapter more discussed on basic mixed-metal oxides (CaO and MgO based), acidic mixed-metal oxides (SiO_2, SnO_2 and Fe_2O_3 based) and acid-base bi-functional mixed-metal oxide ($ZnO–La_2O_3$, $MnCeO_2$ and $SrO–ZrO_2$).[60] Many of the catalysts studied are excellent in the catalytic performance for the biodiesel production through esterification or *in-situ* esterification and transesterification processes.[60] Refaat has briefly presented a review chapter on synthesis methods and characterization of various metal oxides commonly being used in the esterification and transesterification of oil with alcohol for the biodiesel production.[99] The chapter highlighting about the catalytic activity of alkali earth metal oxides, transition metal oxides, mixed metal oxides and supported metal oxides as heterogeneous catalysts in the transesterification reaction. The author has discussed about the catalyst selection and catalyst preparation for efficient transesterification process as well as explained the deactivation issue of the catalyst as important as catalyst activity. The author has concluded about the synergy between emerging technologies as ultra-sonication and microwave irradiation, on one side, and heterogeneous catalysis, on the other side, for the production of biodiesel appears to be very promising.[99] Cardoso et al. [100] have reported a review article about the importance characteristics related to the synthetic route, stability and activity of the tin catalysts in the esterification of triglycerides for biodiesel production with high free acid methyl ester content. They have explained the main structural features and physical properties of the solid tin catalysts such as SnO_2, $SO_4^{2-}–SnO_2$, $SO_4^{2-}–SnO_2–Al_2O_3$, $SO_4^{2-}–SnO_2–Fe_2O_3$ with different Sn to Al and Fe molar ratio, for better understanding and significant contribution for the biodiesel production.[100]

Vedrine has reported a review chapter on the fundamentals of heterogeneous catalysis and on metal oxides special members of heterogeneous catalyst family, acid-base catalyzed reactions, selective partial and total oxidation, de-pollution, biomass conversion and green chemistry including photocatalysis.[61] The main focus of the article is discussion on current industrial applications of supported and non-supported metal oxide catalysts. Chouhan et al. have presented a comprehensive review on a large number of modern heterogeneous catalysts for biodiesel production.[6] The report content discussed on alkali metal oxides, alkaline metal oxides and their derivatives, transition metal oxides, mixed-metal oxides (MMOs), ion exchange resin type oxides, sulfated oxides as solid acid catalysts, carbon and boron group base solids and enzyme based solid catalysts. The authors have discussed on the catalytic activity, selectivity, catalyst loading, catalyst reusability and summary of the future scopes.[6] Diamantopoulos et al. have introduced heterogeneous catalysts as important materials for the biodiesel production.[101] The authors have discussed on zeolite, mixed oxides, sulfonic acid group catalysts, sulfonic acid modified SiO_2, HPAs and polyoxonetalates, supported and substituted HPAs and solid acid catalyst based in waste carbon. They have explained the catalytic activity of these catalysts in terms of their efficiency and reusability. The review revels the fact about the advantages of the solid acid catalysts although they are not much active than base catalysts, benefits such as procedure simplification and positive environmental impacts, support the utility of biodiesel production by using various efficient solid acid catalysts. The lower catalytic activity of the solid acids compared to other catalyst for transesterification reactions is usually compensated by operating at higher calcination temperatures (120–450 °C).[101]

Table 3 summarizing the metal oxides and mixed-metal oxides (MMOs) [73–105] as heterogeneous catalysts for biodiesel production via esterification or/and transesterification reactions.

Hydrotalcites: The hydroxyl carbonates of magnesium and aluminum, hydrotalcites (HTs) are minerals belonging to the family of anionic clays, containing anionic species in the inter-lamellar space. HTs are being used as solid catalysts due to their physicochemical properties, such as thermal stability, porosity, specific large surface area (after calcination), memory effect, basicity or/and acidity, and anion exchange capacity.[106,107] Since last many years, researchers are developing Mg/Al as well as Ca/Al and mixed metal-based HTs materials using various synthesis routes and applied as heterogeneous catalytic materials for base catalyzed organic synthesis.[108,109] Herein, such studies have been noted about the performance of HTs for the biodiesel production.

Xie et al. have developed calcined Mg/Al hydrotalcites as heterogeneous base catalyst by using coprecipitation method for transesterification process of soybean oil and

Table 3: Metal-oxides and mixed-metal oxides as heterogeneous catalysts for biodiesel production using esterification or transesterification reactions.

Sr. No.	Catalysts	Esterification/transesterification reactions molar ratio of oil: alcohol	Ref.
1	Sulphated zinc oxide (SO_4^{2-}-ZnO and SO_4^{2-}/ZnO prepared by coprecipitation and impregnation method respectively	Transesterification of soybean oil Oil: methanol = 6:1	73
2	Lithium-doped ZnO prepared by using impregnation method followed by calcinations	Transesterification of vegetable oil Oil: methanol = 1:12	74
3	CaO–MoO_3-SBA-15 prepared by incipient impregnation method	Transesterification of soybean oil Oil: methanol = 1:50	75
4	Sulfated Fe_2O_3–TiO_2 using conc. H_2SO_4	Esterification of vegetable oil Oil: methanol = 1:20	76
5	Strontium and nickel- oxides prepared by using a co-precipitation method	Transesterification using macaw palm oil Oil: methanol = 1:9	77
6	Cu-nanoparticles impregnated in porous carbon support	Transesterification of pail oil/animal fat Oil: methanol = 1:10	78
7	Dual-acid catalyst sulfur-rich graphene oxide prepared by simple modified Hummer's method	Esterification of oleic acid with methanol Acid: methanol = 20:50 (w/w; g)	79
8	Alkali earth metal oxides (CaO, MgO and BaO) doped SiO_2	Transesterification of vegetable oil/animal fat oil: methanol = 1:16	81
9	Calcium oxide derived from mud clam shell	Transesterification of caster oil Oil: methanol = 1:14	92
10	Ca-doped Ce-incorporated SBA-15 impregnated with CaO. (CaO/CeO_2 and CaO–CeO_2/SBA-15)	Transesterification of palm oil Oil: methanol = 1:20	93
11	SrO–CaO mixed metal oxides	Transesterification of *Jatropha* oil Oil: methanol = 1:10	94
12	CaO/La_2O_3 prepared by co-precipitation method	Transesterification of crude *Jatropha* oil Oil: methanol = 1:25	95
13	Acid-base bi-functional metal-boron catalysts prepared by sol-gel method (metal = Ca^{2+},Al^{3+}, Mg^{2+}, Zr^{4+})	Transesterification of crude *Jatropha* oil Oil: methanol = 1:20	96
14	Mixed metal oxides (CaO–MgO, CaO–ZnO, CaO–La_2O_3 and MgO–ZnO)	Transesterification of high acid *Jatropha* Oil: methanol = 1:25	97
15	Metal oxides (Co_3O_4, KOH, MoO_3, NiO, V_2O_5 and ZnO)	Transesterification vegetable oil with excess methanol	98
16	NaY zeolite-supported La_2O_3	Transesterification of castor oil. Oil: methanol = 1:25	102
17	Alkaline earth metal oxides (BaO, CaO, MgO and SrO)	Transesterification of palm oil Oil: methanol = 1:3 –1:15 (% w/w)	103
18	$CsHPW_{12}O_{40}$, Nb_2O_5, sulfated titania (TiO_2/SO_4^{2-}), sulfated zirconia (ZrO_2/SO_4^{2-}) and SnO_2/SO_4^{2-}	Esterification of dodecanoic (lauric) acid with methanol, propanol, 2-ethylhexanol Acid: alcohol = 1:1 up to 1:5	104
19	ZnO/zeolite and PbO/zeolite prepared by hydrothermal impregnation precipitation method	Transesterification of *Jatropha curcas* and *Pongomia pinnata* oil Oil: methanol (excess) = 1:>3	105

methanol to produce FAME through optimization of reaction conditions.[110] The catalyst calcined at 500 °C with Mg/Al ratio of 3.0 found to be most active having higher basicity and suitable for the reaction having ~67 % FAME conversion. Yagiz et al. [111] have studied catalytic performances of the lipase enzyme immobilized hydrotalcites prepared by co-precipitation method by using commercial zeolites as immobilization materials. The obtained immobilized lipase materials have been used for transesterification reaction of oil. As results, HT was found to be the suitable supporting material for lipase than the other four types of zeolites used and it observed to be able to catalyze the transesterification of waste cooking oil with methanol to produce methyl esters.[111] Mg/Al hydrotalcites prepared by co-precipitation of Mg^{2+} and Al^{3+} ions in alkaline solution of NaOH followed by calcination at 400 °C.[112] The prepared catalyst used biodiesel production from pongamia oil with methanol through transesterification under optimized reaction conditions and resulted ~90 % yield of pongamia oil methyl ester showing potential activity of the present catalyst.[112] The hydrotalcites catalyst with Mg/Al molar ratio of 3.0, calcined at 450 °C under argon (Ar) flow for 6 h has been characterized for spectral analysis.[113] The prepared material has been tested for transesterification reaction of soybean oil with methanol under mild conditions of temperature and pressure to produce biodiesel. The results show highest fatty acid methyl ester conversion of ~94 % at optimized reaction conditions which makes material to be a promising heterogeneous base catalyst for biodiesel formation.[113] Chelladurai et al. [114] have studied an environmentally benign process for the transesterification reaction of neem oil with methanol to yield fatty acid methyl esters (FAME) using Zn–Mg–Al hydrotalcites as heterogeneous solid base catalysts thorough optimization of reaction conditions. The obtained highest triglyceride conversion rate was ~92 % at optimized conditions and this could be attributed to the incorporation of Zn into the Mg–Al hydrotalcite material.

Diserio et al. [115] have reported catalytic performances of Mg/Al hydrotalcites (Pural©MG76) for biodiesel production through transesterification of soybean oil with methanol using both an autoclave and continuous packed bed reactor. The observations confirmed about the calcined Mg/Al hydrotalcites as effective heterogeneous catalyst for the transesterification of triglycerides with methanol where the used catalysts could be regenerated by washing with acetone and reused for the economical way without loss of significant performance.[115] Costarrosa et al. [116] have studied influences of the reaction parameters in terms of response surface methodology (RSM) for the heterogeneous transesterification of waste cooking oil with methanol to produce biodiesel using calcined Mg–Al hydrotalcite catalyst. The study has proved RSM as good indicative tool for predicting the biodiesel yield and also about the calcined Mg/Al hydrotalcites as an effective basic catalyst for the production of biodiesel from waste cooking oil.[116] Mg/Al hydrotalcites has been synthesized by urea hydrolysis and co-precipitation methods and characterized.[117] The prepared material tested for transesterification process of waste cooking oil (a triglyceride) with methanol and optimized the reaction conditions using hexane and glycerol as co-solvents. At optimized reaction condition, Mg/Al hydrotalcites as solid base catalyst gives maximum biodiesel yield and compared with the results of KOH as liquid homogeneous base catalyst.[117] A series of solid base catalysts, KF-doped three-metal mixed hydrotalcites (KF/Ca–Mg–Al) with different cation ratio have been synthesized and applied in transesterification process of palm oil with methanol to yield FAME.[118] The doping of KF and synergetic effect of Ca^{2+} and Mg^{2+} broadly improved the catalytic activity of the HT catalysts. As results, the prepared three-metal mixed hydrotalcites found to be highly active for biodiesel production and obtained ~99 % FAME yield at optimized reaction conditions.[118] The spent catalysts could be regenerated and reused in the transesterification reaction where the FAME yield decreased apparently compared to fresh catalyst due to the fact that the layer structure of the catalyst helped raise the activity of the catalyst.

The Mg/Al based catalysts (double oxides of Mg and Al) prepared by coprecipitation method and characterized for structural properties.[119] The formed double lamellar hydroxides followed by calcination gives double oxides show interesting catalyst properties such as a large superficial area, synergic effect between its elements (which favors the development of the its basic characteristics) and also a shape memory effect, which allows the regeneration of the original structure. The prepared catalysts have been tested through heterogeneous catalytic transesterification reaction of vegetable oil with methanol and resulted in ~97 % FAME formation. The study shows the potential use of the MgAl based hydrotalcites for the biodiesel production and suggesting further structural modification for the improved catalytic activity.[119] Mg/Al hydrotalcites doped with lanthanum and zinc cations with different amounts prepared by using co-precipitation method followed by calcination and the materials have been used as solid base catalyst in transesterification of soybean oil with methanol and *n*-octanol for biodiesel and biolubricants production respectively.[120] The transesterification reaction of canola oil with methanol has been reported using Mg/Al hydrotalcites heterogeneous solid base catalyst prepared by coprecipitation method followed by calcination.[121] The results of the catalytic reaction have been compared with KOH as conventional homogeneous catalyst where the present catalyst found to be less active than KOH.

The potential contribution of Mg/Al hydrotalcites prepared through layered double hydroxide has been reported for the biodiesel production using transesterification of triglycerides.[122] The interesting physicochemical characteristics such as texture and surface morphology as well as basicity of the prepared materials could be modified through synthesis routes and chemical composition. The present report shows useful catalytic characteristic of the hydrotalcites as mixture of mixed oxides catalysts and as supports of active species like alkaline and alkaline earth metals compound.[122] Simonetti et al. have reported use of Ca/Al based hydrotalcites catalysts prepared by impregnation method using KOH solution followed by calcination for the transesterification reaction of soybean oil in methanol and ethanol to produce biodiesel.[108] The catalytic performance of impregnated and non-impregnated catalysts has been compared for the transesterification reaction and as a result, the non-impregnated exhibited with higher activity and hence better performances due to availability of active sites used in the transesterification process.[108] Mg/Al hydrotalcites prepared by co-precipitation followed by calcination and loaded with K_2CO_3.[123] The obtained material used as solid base catalyst for transesterification reaction of *Jatropha curcas* oil with methanol to produce FAME. In the study, spectral analysis confirmed the metal oxide formation which makes catalyst to be highly active and it could produce about ~96 % yield of biodiesel (FAME) under optimized reaction condition.[123] Xue et al. [124] have synthesized activated Mg/Al hydrotalcites NPs by co-precipitation and hydrothermal activation with aqueous $Ca(OH)_2$ solution and characterized its catalytic properties.[124] The prepared Ca-hydrotalcite contained both acidic and basic active sites due to which it could be used for esterification and transesterification of different oils with high acid value. The results show high catalytic activity for production of biodiesel (~93 % yield) from crude oils with high acid value without pretreatment.[124]

Table 4 highlighting the use of various HTs as heterogeneous base catalysts for biodiesel production through esterification or transesterification process of oil with methanol/ethanol using optimization of oil to alcohol molar ratio.[108–124]

Table 4: Hydrotalcites (HTs) as heterogeneous base catalysts for biodiesel production using esterification or transesterification reactions.

Sr. No.	HTs as base catalysts	Esterification/transesterification reactions molar ratio of oil: alcohol	Ref.
1	Ca/Al based HTs (Ca/Al ratio of 2:0) prepared by impregnation method using KOH solution	Transesterification of soybean oil Oil: methanol/Ethanol = 1:30 (~90–95 % FAME conversion)	108
2	Calcined Mg/Al HTs prepared by coprecipitation using alkaline solution	Transesterification process of soybean oil Oil: methanol = 15:1 (~67 % FAME conversion)	110
3	HT-immobilized and zeolites-immobilized lipase enzymatic materials	Transesterification waste cooking oil Oil: methanol = 1:4 (~91 % FAME conversion	111
4	Calcined Mg/Al HTs prepared by coprecipitation using alkaline solution	Transesterification pongamia oil Oil: methanol = 1:6 (~90 % yield of pongamia oil methyl ester)	112
5	Calcined Mg/Al HTs under Ar flow (Mg/Al ratio of 3.0) prepared by coprecipitation using alkaline solution	Transesterification of soybean oil Oil: methanol = 1:20 (~94 % FAME conversion)	113
6	Calcined Zn–Mg–Al HTs	Transesterification reaction of neem oil Oil: methanol = 1:10 (~91 % FAME conversion)	114
7	Mg/Al HTs (Pural©MG76)	Transesterification of soybean oil in autoclave and in a continuous packed bed reactor Oil: methanol = 160 g :160 g (w/w) (~80–85 % FAME conversion)	115
8	Calcined Mg/Al HTs (Mg/Al ratio of 3.1) prepared by coprecipitation using alkaline solution	Transesterification of waste cooking oil Oil: methanol = 1:8 (~95–98 % FAME conversion)	116
9	Calcined Mg/Al HTs (Mg/Al ratio of 3.1) prepared by urea hydrolysis and coprecipitation methods	Transesterification of waste cooking oil Oil: methanol = 1:6 (~78–96 % FAME conversion)	117
10	KF-doped three-metal mixed HTs (KF/Ca–Mg–Al)	Transesterification process of palm oil Oil: methanol = 1:12 (~99 % FAME conversion)	118
11	Calcined Mg/Al based double oxides of Mg and Al prepared by coprecipitation using NaOH solution	Transesterification of soybean oil Oil: methanol = 1:9 and 1:12 (~97 % FAME conversion)	119
12	Mg/Al HTs (Mg/Al ratio of 2.0) doped with lanthanum (La^{3+}) and zinc(Zn^{2+}) cations	Transesterification of soybean oil Oil: methanol = 1:15 (~97 % FAME conversion)	120
13	Calcined Mg/Al HTs prepared by coprecipitation using alkaline solution	Transesterification of canola oil Oil: methanol = 1:6 and 1:12 (~71 % FAME conversion)	121
14	Mg/Al HTs (Mg/Al ratio of 2:3) prepared by layered double hydroxide	Transesterification of triglycerides Oil: methanol = 1:12 (~96 % FAME conversion)	122
15	Calcined K_2CO_3 loaded Mg/Al HTs (Mg/Al ratio of 3:1) prepared by coprecipitation using alkaline solution	Transesterification of *Jatropha curcas* oil Oil: methanol = 1:6 and 1:12 (~96 % FAME conversion)	123
16	Mg/Al hydrotalcites NPs by coprecipitation and hydrothermal activation with aqueous $Ca(OH)_2$	Transesterification of *Jatropha curcas* oil Oil: methanol = 1:30 (~93 % FAME conversion)	124

Metal Organic Frameworks (MOFs): MOFs are porous materials, composed of metal sites and organic linkers, have become a research hotspot due to their exceptional advantages, such as versatile synthetic strategies for controlled morphology, abundant pores, and high surface area.[125] These properties grant MOFs versatile functionalities, which have attracted significant interest from the scientific community in recent years.[125] Their crystalline-to-amorphous nature, consisting of metal ions or clusters linked to organic ligands, offers remarkable surface areas, a high degree of structural diversity, and tunable porosity, making them ideal for a wide range of applications.[125]

With the advantageous character of polyporous materials, MOFs have gained the most suitability for biodiesel synthesis.[126] Molybdenum-MOFs has been synthesized by solvothermal method and applied as catalyst in the esterification reactions of oleic acid and palmitic acid to obtain biodiesel.[127] As a result, a 95 % yield was achieved with the fresh Mo-MOFs, and it was successfully recycled for four cycles, maintaining ~92 % efficiency. A hydrothermal synthesis of chromium(III) nitrate nonahydrate salt with EDTA as an organic ligand has been reported to prepare Cr(III)-EDTA MOF, which demonstrates efficient and promising performance for the esterification of oleic and palmitic acids under mild reaction conditions.[128] Copper(II) based MOFs, Cu-benzenedicarboxylic acid (Cu-BDC), Cu-benzenetricarboxylic acid (Cu-BTC) and MOF-74, provide many active sides that act as Lewis acid species and therefore, used as catalysts in the esterification process of waste cooking oil.[129] The synthesis of 75 % and 50 % oil content with Cu-BDC catalyst converted in FFA content of 5.49 % and 4.826 %, respectively.

2.2 Hydrogen production

Hydrogen (H_2), as a fuel and one of the most extensively studied substitute energy resources for available sources those are being consumed rapidly.[130,131] The combustion of hydrogen can be considered as environmentally benign because it produces only water as by-product, and its adoption as fuel in internal combustion engines, would lead to a remarkable reduction in atmospheric pollution.[132] Now days, hydrogen-based technologies are being proposed for having economically and environmentally efficient system to produce hydrogen such as photo-catalytic water-splitting,[133–137] hydrocarbon decomposition,[138,139] photo-reforming [140–144] aqueous phase reforming,[145–150] and auto-thermal/oxidative steam reforming.[151–153] In this view, mono-metallic, bi-metallic or poly-metallic heterogeneous catalysts based on NPs (oxide supported) are well established catalytic systems for hydrogen production. Several Pd, Pt, Ru, Rh-based heterogeneous catalysts with comparable hydrogen production rate have been reported.

Santo et al. [132] have reviewed the specific catalytic applications of reforming processes such as steam, autothermal/oxidative steam, aqueous phase and dry reforming, catalytic partial oxidations, decomposition, photocatalytic water-splitting and photo-reforming reactions. The authors have reported heterogeneous catalysis based on supported bimetallic NPs, to the reactions favorable for the hydrogen production from the renewable raw materials.[132] They have discussed on advantageous applications of bimetallic versus monometallic catalytic systems, as well as focused on characterizations of structural properties. The correlation between structure and catalytic properties has an influence on the promoter addition. The potential of bimetallic catalyst NPs could be seen from the number of examples of the industrial applications significantly such as hydrogen production using photo-reforming and photocatalytic water-splitting those are discussed in the present article.[132]

Furthermore, metal-supported heterogeneous catalysts can induce changes in the electronic properties of the catalyst surface, offering numerous opportunities for developing advanced catalysts with enhanced catalytic performance.[26] The noble metal catalysts are also interesting aspects of catalysis for hydrogen production through HER because of their ΔG_{H^*} is closed to zero.[154] Zhou et al. have related the catalytic activity with the electronic structure and chemical composition of noble metal-based electrocatalysts.[154] In continuation, a series of lanthanum based heterogeneous catalysts of 1 wt% Pt/$LaMO_3$ where M = Al, Cr, Mn, Fe, Co, Ni has been synthesized and used in the catalytic study of aqueous phase reforming of waste biomass, such as glycerol for sustainable hydrogen production.[155]

Nagaoka et al. [156] have demonstrated hydrogen production by oxidative decomposition of ammonia at room temperature to an acidic $RuO_2/\gamma\text{-}Al_2O_3$ catalyst. In the study ammonia chemisorbed onto $RuO_2/\gamma\text{-}Al_2O_3$ catalyst which further increased the amount of the multilayer physisorbed ammonia which causes strong heat evolution that enables to initiate the oxidative decomposition of the ammonia onto large surface of RuO_2 NPs. The authors have measured and compared the autoignition temperatures of the $RuO_2/\gamma\text{-}Al_2O_3$ and $RuO_2/\gamma\text{-}La_2O_3$ catalysts.[156] As results, on ammonia and oxygen supply to the catalyst at room temperature, it has produced hydrogen along with nitrogen and water vapor. The process requires neither an external energy source nor the use of any complex procedures. The present study briefly introduces a conceptual idea of self-heating of catalysts by adsorption of reactant molecules which is a novel strategy for the cold-start process for hydrogen production from ammonia and other reactions.

Recently, a study discussed the progress and challenges in using non-noble metal cobalt-based heterogeneous supported catalysts, particularly carbon materials, metal oxides, MOFs, and nickel foams, for hydrogen generation from ammonia borane.[157] It provides insights into how the preparation of the electronic and spatial structures of Co-based catalysts can significantly influence the decomposition of ammonia borane for hydrogen generation.[157] Brack et al. [158] have introduced heterogeneous catalysis for the hydrogen production from the hydrolysis process of sodium borohydride ($NaBH_4$). The authors have discussed about the factors affecting the catalytic hydrolysis process of aqueous solution of $NaBH_4$ such as catalyst role, reaction conditions (temperature, time, concentration and volume of $NaBH_4$ and the used stabilizers). The article has brief discussion about the catalysts based on noble metals, mainly focus on Pt and Ru as most efficient at rapid production of hydrogen from the aqueous $NaBH_4$ solution. As noble-metal based catalysts resulting much expensive, transition metal-based particularly Co and Ni-based catalytic system would be a desirable alternative and much more work has been done for the hydrogen generation. Cobalt-borides are found to be emerging catalyst of choice due to low cost and simple synthesis procedures with high catalytic activity leading to maximum hydrogen production yields. They also have explained other transition metal-based as well as metal free-based heterogeneous catalysts for practical applications of the hydrogen generation.[158] Srifa et al. [159] also have studied hydrogen generation by ammonia decomposition using Cs-modified Co_3Mo_3N catalysts prepared by a facile single-step decomposition of a mixture of hexamethylenetetramine and corresponding metal salts under the flow of nitrogen at 700 °C. The kinetic study of the catalytic process shows influence of the presence of the Cs species as it significantly enhanced the catalytic activity of Co_3Mo_3N, an excess amount of Cs could be reduced the activity and hence lower the H_2 production rate. The observed enhancement could be due to electronic modification of Co_3Mo_3N by the electron donation of Cs promoter.[159]

Yan et al. [160] have compared catalytic activities of Ni, Co and W with ZrO_2 support for hydrogen production from PEG-contaminated wastewater by supercritical water gasification process. The results of the analysis show Ni/ZrO_2 exhibits highest hydrogen yields which could be due to catalyst inhibition of toxic intermediate production. The study demonstrated the promising use of Ni/ZrO_2 as heterogeneous catalyst for hydrogen production in a supercritical water gasification process with high activity and stability.[160] Yuranov et al. [161] have developed a heterogeneous catalytic reactor for continuous production of hydrogen via formic acid dehydrogenation. The catalyst support consisting of cross-linked polystyrene beads and polymer electrolyte fuel cell operated on $H_2 + CO_2$ mixtures to produce neat hydrogen. The model presented could help to use formic acid as hydrogen carrier medium and to make maximum industrial application for the sustainable technology. Yamashita et al. [162] have addressed most relevant research approaches in hydrogen generation from two of the most promising hydrogen storage materials such as formic acid and ammonia-borane over carbon supported metal NPs based catalysts. The authors have highlighted recent advancement in mono-metallic and bi-metallic Pd-based and Ru-based catalytic system, also discussed about the important features like nano-particle size, electronic features and composition, functionality of the support and influence of the used additives present in the medium. They have concluded about the prior meet of the high performance heterogeneous catalysts for the hydrogen production with efficiency, economic and reusability.[162] The authors also have reported design and development of efficient Pd-based heterogeneous catalysts supported on carbon or carbon containing materials for the formic acid dehydration process in liquid phase for hydrogen production.[163] They have described important features of metal active phase and catalytic support for finding the efficient catalyst under the optimum experimental conditions. The main issue has been noted about the stability of the catalyst which has to be improved for the practical applications. In this context, modulating the nanoparticle-support interaction could be of great significance in achieving catalysts with notable stability. The incorporation of an adequate heteroatom through doping in the carbon material could be an effective tool to form interesting catalytic system for the current demand through appropriate surface fictionalization. Another way of modification in the synthesis route so that porosity of the carbon material support could be utilized in anchoring and dispersing the metallic active phase would be effective work of interest through which active and durable catalytic system could be developed, and searching useful capping agent to inhibit the nano-particle sintering under using experimental conditions. Also, they have concluded about future investigation to be initiated the use of non-noble metallic NPs as cost effective and durable active catalysts for the hydrogen production from dehydrogenation of the formic acid.[163] Yamaguchi et al. [164] have reported gaseous fuel production from non-recyclable paper wastes such as shredded documents and paper sludge over supported metal catalysts. The gasification catalytic reactions show, a charcoal-supported ruthenium (Ru/C) catalyst found to most active and among to the metal used, the order of the catalytic activity was found to be Ru > Rh > Pt. The gas fuel yield increases by ball-milling treatment of the recycled paper and cellulose powder.[164] The present conceptual technique indicating the possibility of fuel gas production from paper wastes in high-temperature liquid water.

Sikander et al. [165] have introduced scientific approaches reported by researchers for the hydrogen production using HTs based catalysts through describing synthesis methods and structural properties. The authors have briefly explained co-precipitation, urea hydrolysis, microwave treatment and sol-gel method of synthesis for HTs. Various methods of hydrogen production have been discussed such as steam reforming of methane, methanol, ethanol and dry hydrocarbons and partial oxidation of methane. The catalysts, HTs are observed to be more active in almost all hydrogen production processes because of high surface area. Furthermore, the compositional ratios of active metallic cations along with their interaction with the interlayers are a key role for catalytic efficiency.[166,167] Doping of element is another way to enhance the catalytic performance where use of noble metals (Pd,[168,169] Pt,[170] Rh [171]) have been reported successfully. The rigorous operating conditions of hydrogen production processes could damage structural properties of the catalyst, sintering of the cations and deactivation of the catalyst also affects the catalytic efficiency of the HTs. The authors also have developed double layered HT based Mg–Ni–Al catalyst using co-precipitation method by varying Ni content and studied its catalytic performance for the hydrogen production through methane decomposition.[172] The nickel concentration has not been effective to the overall methane decomposition reactions due to the sintering of active sites species leads to depriving of the overall rate of methane conversion. The used catalyst support have played a typical role in the diffusion of the deposited carbon, resulted improved the overall performance rate.

Three metal-based HTs (Ni/Zn/Al-HT) with different Ni/Zn ratios have been prepared by a coprecipitation method and characterized for structural properties where HT and ZnO phases observed along with Zn^{2+} into the layer.[145] The prepared material has been used for hydrogen production via aqueous phase reforming of ethylene glycol and resulting high H_2 generation rate with high selectivity.[145] Ni–Fe mixed oxides obtained from reevesite, a HTs type material prepared by co-precipitation method and tested for steam reforming of ethanol for hydrogen production.[145] The comparative performance of hybrid materials comprising a Ni-based reforming catalyst and HT (Ni-HT) or calcium based sorbents (Ni–CaO/Al_2O_3) has been reported for sorption-enhanced steam methane reforming for H_2 production.[173] The prepared hybrid material (Ni-HTs) exhibited with superior adsorption characteristics and stability compared to powdered mixtures of commercial Ni/Al_2O_3 catalyst and the respective sorbent (CaO).[174] He et al. [175] have studied catalytic performances of noble-metal free-catalyst obtained from Ni/Al HTs for hydrogen production through hydrous hydrazine ($N_2H_4 \cdot H_2O$) decomposition and compared with the ~78 wt % Ni/Al_2O_3-IMP sample. The results show that supported Ni catalyst with a high loading and good dispersion exhibits ~100 % conversion and ~93 % H_2 selectivity for the $N_2H_4 \cdot H_2O$ decomposition at room temperature. The observed activity is due to the cooperation of Ni NPs and strong basic sites which make catalyst as a promising candidate to replace noble-metals for hydrogen production under ambient conditions.[174] Homsi et al. [176] have prepared Co-based HTs (Co_6Al_2 oxide) and thermally stabilized and impregnated using metal precursors of Cu and Ru followed by calcination. The characterization results show formation of CuO, RuO_2, Co_3O_4 and $CoAl_2O_4$ after calcination of the impregnated materials. Both, impregnated and non-impregnated samples have been used for the steam-reforming of the ethanol for H_2 production.[176] As results, Ru with impregnated samples exhibit high catalytic activity compared to Cu-impregnated sample which is attributed to the formation of easily reducible Ru and Co-oxide species at the surface of the support.[176] The authors also have studied catalytic performances of Cu/Co–Mg–Al-based catalysts in the ethanol steam reforming reaction under atmospheric pressure in a fixed catalytic bed reactor coupled to a micro-gas chromatography.[177] From the reaction, H_2 and CO_2 evolved and it increased with the cobalt content and 5Cu/Co_6Al_2 gives very good conversion of H_2 and CO_2. The presence of copper as an active phase has improved ethanol conversion and H_2 production compared to the results obtained in the case of the supports alone. The study leads to develop a catalyst operate at low temperature with high selectivity to avoid formation of by-products.[177] Tuza et al. [178] have reported hydrogen production by aqueous-phase reforming of glycerol using Ni/Cu catalysts derived from HT precursors. The obtained materials have been characterized for structural and surface properties. A clear improvement in the orderliness of the layer has been noted with decreasing copper content and samples with higher amount of copper have larger BET surface areas. The Ni-catalyst without Cu shows high catalytic glycerol conversion observed with good H_2 selectivity and Ni_5Cu catalyst also shows high H_2 selectivity with the smallest amount of CO and CH_4.[178]

The compositional variation and structural advantages such as highly ordered and tunable metal nodes and organic linkers, MOFs enable rapid ion transport and high capacitance. With their abundance of active energy storage sites, MOFs have emerged as attractive candidates to meet the demands of next-generation energy storage technologies in batteries and supercapacitors.[125c] MOFs and their nanocomposites have been widely synthesized, particularly for their potential applications as hydrogen storage materials in proton exchange membrane fuel cells (PEMFCs).[179] MOFs are also of interest as potential materials for use as electrode in lithium, zinc and sodium-ion batteries.[180]

The catalysts used in the hydrogen production process have been summarized[26,132,145,154–182] in Table 5.

Table 5: Hydrogen production using various catalysts.

Sr. No.	Catalysts	Catalytic process	Ref.
1	Supported bimetallic NPs	Photo-reforming and photocatalytic water-splitting	[132]
2	Acidic $RuO_2/\gamma\text{-}Al_2O_3$ catalyst	oxidative decomposition of ammonia	[156]
2	1 wt% $Pt/LaMO_3$ where M = Al, Cr, Mn, Fe, Co, Ni prepared by harsh hydrothermal conditions	Aqueous phase reforming of waste biomass	[157]
3	Noble-metal (Pt, Ru and Rh), transition metal (Ni and co) based catalysts	Hydrolysis process of sodium borohydride	[158]
4	Cs-modified Co_3Mo_3N	Ammonia decomposition	[159]
5	Ni, Co and W with ZrO_2 support (Ni/ZrO_2, Co/ZrO_2, W/ZrO_2)	PEG-contaminated wastewater by supercritical water gasification process.	[160]
6	Different active Ru complexes supports on zeolite ZSM-5, mesoporous MCM-41 silica and functionalized polystyrene beads	Formic acid dehydrogenation	[161]
7	Monometallic and bimetallic Pd-based catalytic systems, (Pd, Pd/Ag, Pd/Au)	Formic acid dehydrogenation	[162]
8	Carbon supported metal NPs	Dehydrogenation of formic acid and ammonia-borane	[163]
9	Charcoal-supported ruthenium (Ru/C)	Gasification catalytic reactions (gaseous fuel production from non-recyclable paper wastes)	[164]
10	Hydrotalcite (HTs) consisting of different metals like Fe, Ni, Cu, Pt	Steam reforming of methane, methanol, ethanol and dry hydrocarbons and partial oxidation of methane	[165]
11	Ce-promoted Ni/Mg–Al catalysts	Dry reforming of methane	[166]
12	HTs supported Pd_2Ga and PdZn intermetallic NPs	Methanol steam reforming	[168]
13	PdZnAl-HTs supported catalyst	Oxidative methanol steam reforming	[169]
14	Ni, Co and pt/hydrotalcites-WO_x	Ethanol steam reforming	[170]
15	Rh-doped Ni/Mg(Al)O catalysts	Methane steam reforming	[171]
16	Double layered HT based Mg–Ni–Al	Methane decomposition	[172]
17	Ni/Zn/Al derived HTs	Aqueous-phase reforming of ethylene glycol	[145]
18	HTs- and calcium-based hybrid materials	Methane steam reforming	[173]
19	Ni/Fe derived HTs	Ethanol steam reforming	[174]
20	Noble-metal-free catalyst derived from Ni–Al HTs	Hydrazine ($N_2H_4{\cdot}H_2O$) decomposition	[175]
21	Ru and Cu supported HTs	Methane steam reforming	[176]
22	Cu/Co–Mg–Al-based catalysts prepared by HTs route ($5Cu/Co_6Al_2$)	Ethanol steam reforming	[177]
23	Ni and Cu supported HTs	Aqueous-phase reforming of glycerol	[178]
24	Prussian blue analogues	Hydrolysis of $NaBH_4$	[181]
25	Fluorine-doped NiO and Ni@C prepared through organic-inorganic hybrid approach	Urea oxidation reaction	[182]

3 Environmental applications

Currently, the problem associated to the energy and environment has no universal solution to solve it. Most of human activities and more, rapidly increasing population and thus, even faster increasing global energy consumption and environmental burdens lead to generate the said unsolved problems. Many more awareness and progressively efforts are being applied to improve the efficiency and accessibility of environmental remediation and Green Chemistry processes. Environmental catalysis certainly plays a typical role in the design and development of efficient processes and technologies to reduce or to minimize waste generation throughout saving energy.[183] Herein, different heterogeneous catalytic systems have been discussed to understand relation between the structure/chemistry and the performance in heterogeneous catalysis which would help to design novel efficient materials for addressing the challenges in potential applications for environmental remediation. These include metal-based and/or metal-free-based catalysts and carbon-based catalysts for green chemistry, semiconductors-based catalysts for photocatalysis and other catalytic systems for environmental technologies.

3.1 Carbon dioxide (CO_2) reduction

Faster deforestation makes sudden increment of CO_2 concentration in atmosphere and thus, global warming problem and climate change become the interest of attention.[150] Therefore, now it is become necessary to find out a significant alternative to capture CO_2 and convert it into useful chemicals and sources of fuel.[183] The availability of the alternative energy source is connected to the source of hydrogen which is carbon neutral and economically feasible. In this view, the hydrogenation of CO_2 to methanol synthesis is providing a renewable or sustainable source of hydrogen.

There has been focused research work on finding selective catalyst that can capture or convert through CO_2 activation under mild reaction conditions with maximum selectivity and yield of methanol. Bahruji et al. [184] have studied structure activity relationship of two series of Pd/ZnO catalysts prepared by immobilization and impregnation methods for direct hydrogenation of CO_2 to methanol. As results, different performances observed for both catalysts prepared by different methods. Pd-NPs deposited through sol-immobilization method which produced active Pd/ZnO NPs catalysts with controlled particle size. It is observed that, high Pd loadings for colloidal catalysts increases methanol formation due to Pd–Zn bimetallic formation and also, methanol production could be reduced at higher temperature due to some sintering effect.[184] A multicomponent Cs-doped $CuO–Fe_2O_3$ supported on Al_2O_3 ($Fe–Cu–Cs/Al_2O_3$) catalyst has been reported for chemical CO_2 recycling by reverse water-gas shift (RWGS) reaction and compared its catalytic activity with that of Fe/Al_2O_3, $Fe–Cu/Al_2O_3$ and $Fe–Cs/Al_2O_3$ catalysts.[185] The addition of Cu to the bare Fe/Al_2O_3 catalyst enhances the activity and selectivity because of Cu–Fe effect and reduced sintering. Similarly, addition of Cs promoter affects the catalytic activity of $Cu–Fe/Al_2O_3$ and thus, multicomponent catalyst $Cs–Fe–Cu/Al_2O_3$ has highest level of CO_2 conversion with full selectivity to CO formation at low temperature. The study reveals the role of promoter added to the catalysts, Cs helps in CO_2 activation due to its basic character in nature through ease of electron transfer from the catalyst to the reactants and facilitation CO_2 adsorption on the catalyst surface. Addition of promoter also helps to suppress the methanation process and it could improve selectivity towards desired product.[185] The study concluding about unexceptional stability and selectivity could be gained through Cs-doped heterogeneous catalytic materials and it suggests using of such materials in gas phase chemical CO_2 recycling. The authors have reported multicomponent Ni-based catalysts supported on Al_2O_3 promoted by the addition of Sn and CeO_2 for the catalytic conversion of CO_2.[185] The results also favoring the earlier study as addition of Sn and CeO_2 promoters have improved the catalytic activity of Ni/Al_2O_3 through enhancement of CO_2 adsorption on the catalyst surface. The presence of CeO_2 enhances the oxygen storage capacity and modified acid/base characteristics of the support lead to improve catalytic behavior over a range of temperatures and space velocities. The catalytic system has also been applied to bi-reforming of methane reaction and significant conversion with stability was observed.[186] The study conducted provides a strategy to design and develop efficient and economic catalyst for practical syngas production form CO_2/CH_4 mixtures. Mutz et al. [187] have prepared bimetallic Ni_3Fe catalyst supported on γ-Al_2O_3 using homogeneous deposition-precipitation method for application in CO_2 methanation and correlate performance and structure of the catalyst. Spectral analysis shows, formation of Ni_3Fe alloy with high fraction of Ni and Fe resulting into small and well defined NPs with controlled particle size and good dispersion. The catalytic performance of the prepared Ni_3Fe has been compared with that of monometallic catalyst of Ni by using a micro-channel packed bed reactor under industrially relevant reaction conditions. As results, Ni_3Fe exhibited with improved performance to have conversion of CO_2 about ~71 % selectively for methanol production and most important about retained a high stability. The study indicating importance of synergetic effect of Ni and Fe due to which catalyst has excellent performance and stability.[187] Cobalt catalysts supported on ZrO_2 (Co/ZrO_2) and Al_2O_3 (Co/Al_2O_3) prepared by impregnation with different metal loadings show good catalytic activity for CO_2 methanation.[188]

Veselovskaya et al. [189] have studied direct air capture/methanation process over the commercial nickel methanation catalyst NKM-2V which is effectively combine CO_2 capture from ambient air and convert it into methane by Sabatier reaction. The experimental analysis showing enhancement of CO_2 to CH_4 conversion with increase of temperature and decrease in CO_2:H_2 ratio. The Sabatier process also performed well in the two reactor system using K_2CO_3/Al_2O_3 material for direct capture of CO_2 from ambient air and the commercial nickel catalyst for methanation of CO_2 via Sabatier process. Wu et al. [190] have studied influence of formate ($HCOO^-$) coverage on the reaction rate of methanol synthesis from CO_2 hydrogenation over Cu (2 1 1) with the coverage-dependent adsorbate-adsorbate interactions. The study shows, increasing formate coverage would destabilize the adsorption of the reactant molecules/reaction intermediates and transition states. Turn over frequency varied at different coverage of surface species under the same reaction condition. The combination of HCOO and HCOOH hydrogenation steps could be a rate-determining step and thus, methanol formation could be controlled through surface coverage of formate and the effective free energy barriers.[190] Han et al. [191] have prepared Au nano-clusters with different particle size (average ~2 *nm*) on various supports (ZnO, CeO_2, TiO_2, ZrO_2) and studied their catalytic performance on direct hydrogenation of CO_2 to methanol under solvent free condition. Among the all catalysts prepared, Au/ZrO_2 with 1.6 *nm* particle size exhibits highest catalytic activity and selectivity towards methanol formation at low temperature, mainly because of small particle size and appropriate coupling between the Au particles and support in the catalyst.[191] Williams et al. [192] have prepared unsupported bimetallic Pd–In NPs by using thermal decomposition of Pd and In precursors in high boiling point solvent followed by reduction using dilute hydrogen gas. PdIn NPs catalyst has been tested for liquid phase methanol synthesis process and found to be most efficient catalyst showing ~70 % higher methanol production rates compared to conventional catalysts such as $Cu/ZnO/Al_2O_3$.[192] Rao et al. [193] have studied fundamental physicochemical properties of CeO_2 to improve its catalytic activity for energy and environmental applications. In the study, shuttle-shaped CeO_2 prepared under hydrothermal condition by homogeneous precipitation method and the material shows good surface area and low temperature reducibility which show superior CO oxidation efficiency as environmental application. The linear sweep voltammetry, chronopotentiometry and CO stripping voltammetry studies show that CeO_2 provides higher number of labile OH_{ads} species through active triple-phase interfacial sites for facile oxidation of CO_{ads} on Pt/C as energy application.[193] The study set a significant potential and anti-poisoning effect of CeO_2 to Pt/C for electro-oxidation of ethanol in acidic media. Arena has reported the composite $MnCeO_x$ system having high redox activity, surface amphoteric behavior and good chemical stability as a viable alternative to highly-cost noble metals for a variety of environmental catalytic applications.[194] These include a range of applications such as the detoxification treatment of industrial wastewater; the abatement of pollutants in gas exhausts; and bio-15 fuel and fine-chemicals synthesis manufacture.

Jadhav et al. [195] have discussed about the recent advanced studies of last decade on catalytic CO_2 hydrogenation to methanol. They have explained the importance of the various novel synthesis routes like solid-state reaction, ultra-nitrate combustion and reveres co-precipitation under ultrasound irradiation to prepare $CuO/ZnO/ZrO_2$ heterogeneous catalysts.[195] The main focus was CuO/ZnO-based catalyst promoted with Pd and Ga for CO_2 hydrogenation to methanol. As discussed earlier in the text, addition of Pd and Ga promoters enhances the catalytic activity, stability and selectivity of CuO/ZnO catalyst, *i.e.*, Pd/ZnO [196] and Ga promoted Pd/SiO_2,[197] show excellent catalytic behavior. Authors also have discussed two pathways of catalytic hydrogenation of CO_2 to methanol; one is a RWGS and another, through mechanism of formate ($HCOO^-$) intermediate formation.[195] They have concluded, among the available alternate catalytic techniques for methanol synthesis from CO_2 dehydrogenation via RWGS reaction would be promising tool. Porosoff et al. [198] have demonstrated the possible use of a low-cost non-noble metallic material Mo_2C (molybdenum carbide) as an active and selective heterogeneous catalyst for conversion of CO_2 using hydrogen. The spectral analysis shows that carbide is preliminary active phase of Mo_2C while oxide form was observed throughout the reaction. Mo_2C catalyst has ability to break C=O bond of CO_2 and to dissociate hydrogen to either perform hydrogenation of CO_2 or remove oxygen from $Mo_2Cz–O$ intermediate, thus, this way catalyst could show its dual functionalities which makes it suitable for CO_2 activation.[198] The present catalyst preparation is much lower cost make possible to set a large-scale catalytic CO_2 conversion process. Waclawek et al. [2] have discussed the mechanism of heterogeneous catalysis and advances in its development for environmental applications. They also have introduced a heterogeneous catalysis as an important aspect of the chemical process, from the synthesis methods and characterization techniques through surface morphology. The authors have highlighted the challenges about to improve spectroscopic and microscopic techniques to provide structural information such as chemical composition, size and shape of metal-NPs and gas phase concentrations in a spatially and time-resolved manner. They have suggested, industrial chemistry needs to combine all of these things together to understand the solid handling, chemical reaction, energy engineering, and heat and mass transfer of these catalytic processes. Theoretical scientist and physicist would have good partnership to make possible to design and develop superior catalytic systems for inexpensive fuel-cell vehicles.[2]

Yan et al. [199] have provided detailed overview of the development of nickel-based bimetallic catalysts for chemical and electrochemical processes such as catalytic reforming, dehydrogenation/hydrogenation and electrocatalysis for energy production and environmental remediation. The authors have discussed the role of bimetallic surface and each metal counterpart of the reactions, and the surface activity relationships which are typical part of catalytic performances. They have explained diffusion rate of Ni which is the major issues related to the catalyst activity and stability under the different reaction conditions like high temperature for reforming condition. On point of view, to develop cost effective catalysts without compromising their activity and stability, it could be possible by alternative way of introduction of non-metal elements such as boron and phosphorous and already nickel-borides and phosphides could further improves the catalytic behavior for the desired applications.[199] Labhasetwar et al. [200] have studied a number of perovskites based on Co, Mn, Ru, and Fe and their substituted compositions. The prepared perovskites catalysts show good redox properties, the promotional effect of co-ions, and the increased exposure of catalytically active transition metals in certain preparations. The catalysts exhibited enhanced catalytic activity for diesel soot oxidation, three-way catalysis, NO decomposition, low-temperature CO oxidation and oxidation of volatile organic compounds.[200] Wang et al. [201] studied the physicochemical properties of fly ash exhibiting strong thermal stability and characteristic of a catalyst support. The fly ash supported catalysts have shown a very good heterogeneous catalytic activity for a variety of catalytic reactions as H_2 production, CO_2 reforming of methane, NH_3 decomposition, catalytic reduction of NO_x and SO_x, methane oxidation, dye decomposition, petroleum hydrocaracking.[201]

MOFs have also been reported to be efficient photocatalyst [202] and electrocatalysts [203] for CO_2 capture. Cobalt–porphyrin MOF has been examined for selective reduction of carbon dioxide to carbon monoxide in aqueous electrolytes with the 76 % yield and stability over 7 h with a per-site turnover number of ~1,400.[204b] A case study on Bi-based MOFs has been reported for electrochemical CO_2 reduction and as results excellent activity, selectivity, and durability for formate production.[204c]

Table 6 contains various catalytic systems for CO_2 reduction [184–206] as environmental application.

Table 6: Catalytic CO_2 reduction using various catalysts.

Sr. No.	Catalysts	Catalytic process	Ref.
1	Pd/ZnO	Direct hydrogenation of CO_2 to methanol	180
2	Cs-doped CuO–Fe_2O_3 supported on Al_2O_3 (Fe–Cu–Cs/Al_2O_3)	Reverse water-gas shift (RWGS) reaction	181
3	Ni-based catalysts supported on Al_2O_3	Catalytic conversion of CO_2 and bi-reforming of methane, syngas production form CO_2/CH_4 mixtures	182
4	Ni_3Fe catalyst supported on γ-Al_2O_3	CO_2 methanation	183
5	Cobalt catalysts supported on ZrO_2 (Co/ZrO_2) and Al_2O_3 (Co/Al_2O_3)	CO_2 methanation	184
6	Commercial nickel methanation catalyst NKM-2V	Direct air capture/methanation process	185
7	Cu(211)	Hydrogenation of CO_2 to methanol	186
8	Au nano-clusters with different particle size (average ~2 nm) on various supports (ZnO, CeO_2, TiO_2, ZrO_2)	Direct hydrogenation of CO_2 to methanol	187
9	Unsupported bimetallic Pd–in NPs	Liquid phase methanol synthesis process	188
10	CeO_2 (cerium oxide)	CO oxidation	189
11	Composite $MnCeO_x$	Redox process	190
12	Carbon nanotube-supported Pd/ZnO	Hydrogenation of CO_2 to methanol	192
13	Ga promoted Pd/SiO_2	Hydrogenation of CO_2 to methanol	193
14	Mo_2C (molybdenum carbide)	Hydrogenation of CO_2 to methanol	194
15	Nickel-based bimetallic catalysts	Hydrogenation of CO_2 to methanol	195
16	Fly ash supported catalysts	CO_2 reforming of methane	197
17	Cobalt–porphyrin MOFs	Selective reduction of carbon dioxide to carbon monoxide in aqueous	199
18	Bi-based MOFs	Electrochemical CO_2 reduction	199
19	NNU-29 (polyoxometalate-based MOFs)	Photoconversion CO_2 to formate	200
20	Postsynthetic exchange (PSE) of Ti(iv) into a Zr(iv)-based MOF	Photocatalytic CO_2 reduction to HCOOH	201
21	Bimetallic (Zr/Ti)-MOFs	Photocatalytic CO_2 reduction to HCOOH	202

3.2 Degradation of organic pollutants

Rapidly developing industrial activities produce huge amount of organics containing non-degradable solid wastes which are spread out in the open environment and further contaminates groundwater and surface water as well as air. The major contamination produces from petroleum refining, petrochemicals, pharmaceuticals, dye, paper, plastic, dairy production, fertilization and pesticide chemical industries etc.[207–209] Many reports are published related to develop effective process and technologies for wastewater treatment and oxidation process to decompose toxic and hazardous impurities at low cost and high efficiency. The literature on heterogeneous catalysis opens the ways about to use of novel catalytic systems for the decomposition of organic wastes from the aqueous solution as well as conversion of toxic gaseous pollutants to harmless products.

The most preferred catalytic systems are those based on photocatalysis with advanced oxidation processes (AOPs), as they offer the potential to utilize naturally available and renewable solar energy as a light source for photochemical waste remediation, making the process both green and sustainable.[209] Among AOPs, semiconductor-mediated photocatalysis has proven to be highly effective, as it completely mineralizes contaminants present in either the gas or liquid phase.[210,211] In these intriguing and effective fields of innovation, TiO_2 photocatalysis and the photo-Fenton process are two well-established AOPs. As a result, there are a significant number of literatures on their environmental applications, such as water and air decontamination, as well as self-cleaning surfaces.

Merouani et al. have explored the use of AOPs, particularly for environmental remediation, followed by photoactivated processes.[14–17] In these studies, authors have developed a number of active radicals to facilitate the formation of reactive species for the degradation of toxic dyes such as chlorazol black,[14a] Allura Red AC,[14b] Safranin O,[14c] textile dyes and organic contamination.[15] The authors also applied the combined use of heterogeneous photocatalysis with high-frequency ultrasonic irradiation for dye and phenol degradation.[16,17] It was observed that the solar photocatalytic process operated efficiently, even when the pollutant was present at high concentration levels. It could be attributed to the occurrences of synergistic effect strongly dependent on the initial substrate concentration.[212]

Duan et al. [213] have discussed AOPs as effective technique for activating superoxides radicals for degradation of organic pollutants in aqueous systems. Magnetic (Fe_3O_4) carbon supported manganese oxides (Fe_3O_4/C/Mn) have been used as an effective catalytic system for phenol degradation through peroxymonosulfate (PMS) activation.[214] In the catalytic system, radical generation takes place due to redox process of Mn^{4+}/Mn^{3+} and magnetic support helps for catalyst separation. The catalyst $CoFe_2O_4$, prepared from Co–Fe alloys for the catalytic oxidation process via PMS activation to generate sulfate radicals.[215] A catalytic system, Ce–Mg/Al_2O_3/ozone has shown good efficiency for decomposition of resistant petroleum organic wastes.[216]

Mesoporous CuO/TiO_2 nanotubes and CuO nanorods-reduced graphene oxide prepared for catalytic oxidation of air pollutant CO to CO_2.[217] Mixed metal oxides of Fe–W–Ce [218] and V_2O_5–WO_3/TiO_2,[219] used for conversion of NO_x with NH_3 into N_2 and H_2O. Oxidative dehydrogenation of ethane to ethylene and reduction of N_2O could be simultaneously performed by using Cr/Al_2O_3,[220] as well as N_2O has been directly decomposed on Cu–Zn/$ZnAl_2O_4$ and Zn/γ-Al_2O_4.[221]

Wang et al. [222] have prepared red mud supported Co-oxide based catalysts as significantly effective for phenol decomposition via PMS activation. The authors also have reported natural zeolites supported Co oxide catalysts for phenol degradation through oxidation and adsorption process.[223] Sharma et al. [224] have demonstrated heterogeneous Fenton or Fenton-like reactions like H_2O_2–Fe^{3+} (solid)/nano-zero-valent iron/immobilized iron and electro-Fenton-pyrite for decomposition of dyes and phenols.

Wang et al. [225] have prepared MnO_2 nanoparticles as α-, β- and γ–MnO_2 obtained as nanowires, nanorods, and nanofibres respectively. The prepared catalysts were tested for phenol degradation and α–MnO_2 was found to be more effective and stable in term of recyclability for phenol decomposition. They also have reported a comparative study of Mn_3O_4, Co_3O_4 and Fe_3O_4 nanoparticles for decomposition of phenolic contamination in aqueous solution. The catalysts are found to be effective in heterogeneous activation of PMS to produce sulfate radicals for phenol degradation and the order of catalytic activity was observed as $Mn_3O_4 > Co_3O_4 > Fe_3O_4$.[226] Powder activated carbon materials have been reported as green heterogeneous metal-free catalysts for the degradation of phenol through generation of sulfate radicals.[226] The degradation study shows that activated carbons were significantly effective with PMS to produce sulfate radicals compared to use with H_2O_2 and peroxydisulfate.

Galeano et al. [227] have briefly introduced mixed Al/metal-pillared clays as effective catalytic system for the degradation of organic pollutants in aqueous streams. The prepared catalytic system using Fe, Cu and Mn show metal pollution prevention and an effective performance under operative conditions. Al/Fe-pillared clay has been exhibited as most active catalyst for catalytic wet peroxide oxidation (CWPO) process and possesses desirable features of a catalyst able to operate the CWPO detoxification over a wide variety of real wastewaters.[227] Nair et al. have evaluated catalytic activity of Mn-substituted zinc nanoparticles ($Mn_xZn_{1-x}Fe_2O_4$) prepared by sol-gel method.[228] As results, catalyst found to be very active wet peroxide oxidation of *p*-chlorophenol. Zhang et al. have evaluated catalytic performance of acid-modified coal fly ash catalyst for a Fenton-like process in *p*-nitrophenol wastewater treatment.[229] Zhen has briefly reviewed on cobalt oxide (Co_3O_4) [230] as environmental catalysis for catalytic reduction of NO by ammonia, hydro-desulfurization of COS, ozonation degradation of phenol, photocatalytic degradation of selective hydration of aromatic nitriles,[231] oxidative dehydrogenation of propane,[232] oxidative dehydrogenation of cyclohexane,[233] and hydrogen production by photo-catalytically.[234] Kumar et al. [235] have introduced various synthesis routes for aerogels and metal-organic framework as well as potential utilities as heterogeneous catalysts for environmental and energy applications. These include removal of heavy metals, CO_2 capture and reduction, photodegradation of pollutants, air cleanup and water splitting as environmental and energy production through hydrogen, methane reforming, CO_2 conversion and NO_x removal as energy applications.

So far we have discussed on advanced oxidation processes (Fenton process, ozonation, sonolysis etc.) to reduce/control the organic pollutants from the aqueous and air, where active radicals involve in decomposition of large polluting molecules to small harmless molecules. Besides use of such heterogeneous catalysis, photocatalysis gaining huge attention with significant advancements being made in the synthesis of novel catalytic materials and nano-structures, and the design of efficient processes for the degradation of aqueous as well as atmospheric organic pollutants. Thus, photocatalysis is considered to be the most practical tool due to its usage of sunlight to decompose organic pollutants to convert them into valuable chemicals. A number of semiconductor-based (TiO_2, CdS, CdSe, ZnO, SiO_2, ZrO_2 etc.) photocatalysis are now well established and are being employed as environment-friendly catalytic process.

Many researchers are engaged to design novel photocatalyst by considering the current environmental challenges and providing a clean and sustainable photocatalytic system. Dong et al. [236–238] have reported photocatalytic NO removal by using O/La co-functionalized amorphous graphitic carbon nitride ($g–C_3N_4$) which shows good efficiency. The incorporation of O and La form interlayer induce electron transportation which could reduce energy barriers and hence enhanced photocatalytic activity. The authors also have reported photocatalytic activity of Sr–intercalated $g–C_3N_4$ for oxidation of NO to convert non-toxic molecules selectively for air pollution control.[238] O/Ba co-functionalized amorphous carbon nitride system has exhibited enhanced photocatalytic NO removal rate with good selectivity to produces NO_2^- and NO_3^- while it also preventing the generation of toxic intermediate NO_2. The authors also have prepared thermally and chemically stable Bi_3WO_6 tested for photocatalytic NO oxidization.[239] The presence of oxygen vacancy narrows the band gap and also promotes visible light absorption hence; the enhanced activity was observed.

Particularly, CdS as a photocatalyst has gained extensive interest due to its relatively narrow band-gap for visible-light absorption and sufficiently negative potential of the conduction band edge for the reduction of protons.[240] Generally, CdS is one of the most prominent semiconductors as a visible-light-responsive photocatalyst with a band gap of 2.4 eV among the other photocatalyst being used for hydrogen production. Cheng et al. [241] have introduced CdS and CdS–based photocatalyst that possess excellent photocatalytic activity in terms of solar-fuel generation and environmental cleaning through degradation of pollutants, hydrogen production and reduction of CO_2 to hydrocarbon fuels. The monovalent CdS nanoparticles with different crystal forms (*wurtzite* phase and *zinc blende* phase) have been evaluated for the hydrogen production.[241] Zhang et al. have prepared CdS nanorods by a one-step solvothermal method and obtained an excellent photocatalytic activity for H_2 production with a high dispersion of Pt.[242] There are many studies reported on binary CdS-based photocatalytic nano-composite materials such as CdS/ZnO,[243] CdS/TiO_2,[244,245] and CdS/graphene,[246] CdS/sulfides (CdS/CuS),[247] CdS/ZnS,[248] Bi_2S_3/CdS [249,250] and, CdS/WS_2,[251] MoS_2/CdS,[252] for H_2 evolution. The main advantage of the combination of such nano-composite construction is to improve photochemical properties and crystal forms of CdS and also increase the photogenerated electrons for photocatalytic H_2 production. Recently, researchers have made efforts to combine CdS with other two co-catalysts to form ternary CdS-based photocatalysts such as CdS/WS_2/graphene,[253] CdS/MoS_2/graphene,[254–256] CdS/$g–C_3N_4$/CuS,[257] CdS/Ag_2S/carbon-nano-tube (CNT),[258] CdS/WC/TiO_2,[259] and CdS/MoS_2/TiO_2.[260] The photocatalytic hydrogen production was enhanced by using these ternary CdS-based photocatalysts and also preventing photo-corrosion.

Beside use of CdS for photocatalytic H_2 production, it also makes significant contribution for environment cleaning as well as energy storage through conversion of carbon dioxide (CO_2) to produce useful hydrocarbons such as methane, methanol, formic acid and formaldehyde etc. The reduced graphene oxide/CdS nano-rods composite exhibits very good photocatalytic activity for conversion of CO_2 to methane where graphene oxide act as photoelectron acceptor and thus reduced recombination rate of photogenerated electron-hole pairs and hence enhanced photo-response.[261] CdS-based, CdS/$ZnIn_2S_4$,[262] nano-composite and CdS/TiO_2,[263] nano-tube array has been exhibited with efficient dye degradation under visible irradiation and under sonication respectively.

TiO_2, as an extensively studied and robust material in the field of photocatalysis research, as it was beginning from 1972 Fujishima and Honda et al., about the noble work of H_2 production from water splitting.[264] TiO_2 nanoparticles have wide range of applications and acts as back bone for many advanced process and devices such dye sensitized solar cells, sensors and rechargeable batteries/super capacitors etc.[265,266] Many more applications have already been well set for commercial productions like biomedical devices and drug delivery which has made TiO_2 itself undivided part of photo-induced processes. Many researchers have reviewed about possible surface and structural modification for TiO_2 and also about their catalytic mechanism revel more interesting facts about TiO_2 photocatalysis.[244,266–268]

Among all the possible applications of TiO_2 as photocatalyst, it has been extensively used for photodegradation of various pollutants. It is very interesting to study about TiO_2 semiconductor based photocatalytic mechanism upon absorption of photons and generation of reactive radical species through electron-hole pair recombination process. The pure mesoporous TiO_2, TiO_2 -nanorods and -nanotubes have been demonstrated for their excellent photocatalytic activity for degradation of organic pollutants under suitable conditions.

In addition, progressive performances continuing through surface modification into TiO_2 by doping metal and non-metals which enhance visible light adsorption. Recently we have reviewed on the possible surface modification into TiO_2 photocatalysts as well as including development of Plasmonic photocatalyst.[245b]

As part of environmental catalysts, MOFs also have been explored for air and water environmental remediation processes including removal of toxic metal ions, photocatalytic degradation of toxic dyes and other organic pollutants.[269] Recently MOFs of MIL-125(Ti)–NH_2, MIL-125(Ti) and MIL-125(Ti)-$(NH_2)_2$,[270] UiO-66 and UiO-66-NH_2,[271] MOF-5,[272] NH_2–UiO-66(Zr) ,[273] NH_2-UiO-66(Hf) [274] and HKUST-1 [275] are considered to have good to excellent gas adsorption capacity.

4 Major challenges for heterogeneous catalysis

Since over the many decades, catalysis researchers have been at the lead in addressing numerous challenges in generation of efficient energy resources, controlled on pollution, and sustainable development. The advanced strategies and approaches being developed by the catalysis community have led to significant changes, contributing to economic growth.

At the core of these efforts, heterogeneous catalysis offers low cost, high conversion efficiency, and product selectivity, enabling a wide range of industrial processes to proceed effectively. The recyclability of heterogeneous catalysts promotes green and sustainable manufacturing while preventing secondary pollution. From an economic perspective, the Heterogeneous Catalyst Market was valued at USD 24.6 billion in 2023 and is expected to register a compound annual growth rate (CAGR) of over 4.8 % between 2024 and 2032.[276] More than 80 % industries such as petrochemicals, chemicals, and refining continue to expand globally; the demand for heterogeneous catalysts is increasing.

However, applying heterogeneous catalysis on an industrial scale presents a exclusive set of challenges that can influence efficiency, cost, and sustainability. Therefore, its advancement requires the search for new materials with optimal catalytic activity and economic feasibility. In many important cases, catalyst deactivation often leads to a reduction in overall catalyst performance due to substantial or complete blocking of surface sites, carbon deposition, pore plugging, and the destruction of the catalyst. Catalyst deactivation (nonselective and selective deactivation) must be estimated in an industrial unit using temperature profiles, which can then guide decisions regarding improved process control and timely catalyst replacement.

The efficiency of a heterogeneous catalyst is strongly dependent on the ability of reactants to reach and interact with active sites on the catalyst surface. In the context of biodiesel production, the catalyst surface should exhibit hydrophobic properties, such as mesoporous surface reactivity, which helps facilitate the adsorption of oily hydrophobic species onto the catalyst's surface. Therefore, the hydrophobicity of acid sites has become a key focus, as it minimizes poisoning by polar molecules. In case of high temperatures, catalyst may undergo structural changes leading to further loss of catalytic activity, compromising the process efficiency and leading to potential process failures. Developing and testing catalysts with sustainable thermal stability is essential for applications that involve high temperatures. Another important issue is translating a catalytic process from the laboratory to an industrial scale. Heat and mass transfer conditions are not identical at both scales, so scalability must be carefully considered for successful industrial application.

In general, variations or modifications in synthetic methods that controls the physico-chemical and thermal characteristics of heterogeneous catalysts that can lead to significant changes in reactivity and selectivity of the catalyst. Thus, we have to continue to design and modify new with the present characteristics to understand the interaction of the whole catalytic system. Additionally, understanding the effects of reaction conditions on the catalyst at a molecular level still requires the assistance of advanced, predetermined technologies. In this regard, computational screening technology can be a viable solution, providing acceptable estimations of surface reactivity with relatively low-cost information.

5 Conclusions

The present review article providing a prior literature on advancement of heterogeneous catalysis with its environmental and economic benefits in the field of energy generation and sustain the available feedstock as well. The varieties of materials have been discussed to explore theirs possible utilities as an emerging aspect of the materials science. Heterogeneous catalytic systems such as solid acids (H-form zeolites, sulfated-oxides, sulfonic ion exchangers, mesoporous silica materials, zirconia and titania supported materials), solid bases (β-zeolites, hydrotalcites, alkali metal- and mixed metal-oxides), transition metal based-MOFs catalysts are playing key role for biodiesel production as an alternative fuel source. As a part of heterogeneous catalysis, photocatalysis has major contribution for the environment remediation and exhibits as a promising green approach for the future demand with further investigation.

The present report could help to rational design a novel material by tuning the surface morphology and structural properties, and hence an efficient and non-expensive catalytic system as a part of eco-friendly way out to overcome the present challenges. The further progress in the heterogeneous catalytic systems will facilitate alternative fuel production and thus they can substitute the present expensive and hazardous catalytic systems.

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