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Types and Concentrations of Catalysts in Chemical Glycerolysis for the Production of Monoacylglycerols and Diacylglycerols

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Monoacylglycerol (MAG) and diacylglycerol (DAG) are structured lipids that have been widely used in various pharmaceutical, cosmetic, and food industries. MAG and DAG are generally produced by chemical glycerolysis. Chemical catalysts have been shown to be more efficient, economical, and effective. This study summarizes and discusses the factors that affect the synthesis of MAG and DAG by chemical glycerolysis, such as temperature, reaction time, and type and concentration of catalysts that affect the resulting MAG and DAG concentrations. Homogeneous catalysts such as KOH and NaOH are very effective for generating MAG and DAG conversions up to 91%, but they have a disadvantage, mainly because they cannot be used repeatedly. However, heterogeneous catalysts have great potential to be developed into catalysts with high activity, environmentally friendly, and can be used repeatedly.

1. Introduction

The need for emulsifiers is increasing along with the development of emulsion-based food products, especially emulsifiers from the mixture of monoacylglycerols and diacylglycerols, which are the most considerably used in the food industry, which is about 75% [1]. Commercially, MAG and DAG are used in food products such as cake products, butter, margarine, and confectionaries because they have good emulsification, stabilization, and conditioning properties [2,3]. Mono and diacylglycerols are also used in the pharmaceutical, cosmetic, textile, and plastic industries in consequence of their plasticizing and lubricating properties [4,5]. Applications of MAG and DAG in various products can be seen in Table 1.

Naturally, MAG and DAG are minor components in various vegetable oils with a maximum content of 10% [6]. MAG consists of three isomers, namely enantiomers (sn-1 and sn-3) and regioisomers (sn-2) [7]. DAG be composed of 2 fatty acyl chains, which are esterified into glycerol backbone and can have the shape of 1,3-DAG and 1,2 (or 2,3)-DAG [8]. MAG and DAG are non-ionic molecules that have a free hydroxyl group, which is a hydrophilic group, and a fatty acid ester group, which is a lipophilic group [9]. The double affinity of MAG and DAG or often called amphiphilic, means that they can be used as emulsifiers. MAG with one fatty acid group and two free hydroxyl groups on glycerol makes it behave like fat and water. MAG is an emulsifier that is not very sensitive to acidic conditions. The way the emulsifier works is by lowering the surface tension between the two phases and then stabilizing the products [10].

Commercially, the synthesis of MAG and DAG can be conducted by various methods, namely glycerolysis, direct esterification, and partial or alcoholic hydrolysis [5]. Various types of catalysts are also used, such as homogeneous base catalysts, heterogeneous bases, homogeneous acids, and heterogeneous acids. Several studies have shown a relatively high yield when using a homogeneous base catalyst and a heterogeneous base catalyst, while acid catalysts produce a relatively lower yield. In general, the synthesis of MAG and DAG on a large scale is carried out using the chemical glycerolysis method of oil, which is reacted with glycerol using an alkaline catalyst (such as NaOH and KOH) at high temperatures [2,11].

Table 1: Applications of MAG and DAG in Various Products.

Source of MAG/DAG	Products	References
Palm-based oils/fats	Emulsifier	[12]
Palm oils	Emulsifier	[13]
Vegetable oil	Emulsifier	[14]
Palm mild fraction	Shortening	[15]
Sunflower oil, palm kernel olein	Margarine	[16]

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Chicken fat	Structured fat	[17]
Corn oil	MAG-DAG Oils	[18]
Vegetable oils	MAG-DAG Oils	[19]
Palm olein	MAG-DAG Oils	[20]
Monostearate	Oleogels	[21]
Monostearate, monopalmitate	Organogels	[22]
Saturated fat	Organogels	[23]
Saturated fat	Oleogels	[24]

Chemical glycerolysis at high temperature has several disadvantages, such as dark-colored products and high energy consumption. Several studies have reported that chemical glycerolysis of oils and fats can produce MAG and DAG of about 45-55% and 38-45%, respectively [3]. Subsequent molecular distillation is required to acquire monoacylglycerols with a purity of 90% [25], needed for the pharmaceutical, cosmetic, and food industries. Recent research studies about the glycerolysis reaction at low temperatures using a solvent or without a solvent; the concentration of MAG and DAG generated by this reaction ranges from 40-80% [26].

Another alternative used to substitute chemical catalysts is to use enzyme catalysts [27]. However, the use of enzymes has several drawbacks, such as the glycerolysis reaction requires special conditions and slow reaction kinetics. Besides, the high price of enzymes is a consideration for industrial applications [4]. The use of cheap and easy to obtain raw materials is an important factor in the manufacture of MAG and DAG on an industrial scale. Over the past few years, means have been made to produce high MAG using chemicals and enzymes as catalysts, and methods have been promoted with the aim of increasing the yield of MAG and DAG [28].

Various methods and various types of catalysts can be used to produce MAG and DAG, which can be applied to various food industries. This study discusses the effect of various types of chemical catalysts and their concentrations on the production of MAG and DAG using the glycerolysis method by considering other factors such as the molar ratios of oil to glycerol, temperature, and reaction time. In addition, the NaOH catalyst, which is a homogeneous catalyst, has not been widely discussed, so it is interesting to study in-depth because it has high catalytic activity and is efficient.

2. Characteristics of Mono- and Diacylglycerols

MAG and DAG are non-ionic molecules that have hydrophilic and hydrophobic groups [9]. MAG is an anionic emulsifier with excellent emulsifying properties because it has two hydrophilic groups (hydroxyl) and one hydrophobic group on the fatty acid chain. These emulsifying characteristics are used in food products, cosmetics, plasticizers, detergents, and pharmaceutical formulations [29]. On the other hand, DAG can be used as an emulsifier, especially in emulsion systems of water in oil (o/w). DAG can also effectively prevent the accumulation of fat and diseases related to obesity, so it is often used as a functional ingredient and including lipids that are good for health [30].

MAG and DAG are needed in almost all types of food products. Its main use includes bakery products, margarine, convenience foods, and frozen desserts. MAG and DAG are used as part of fat products and are often associated with other emulsifiers. Lipophilic characteristics cause MAG and DAG to have excellent properties as emulsifiers in water in oil (w/o) system, as required in the manufacture of margarine and shortening [15,16,31].

One of the uses of MAG and DAG is as an emulsifier. The use of emulsifiers is to maintain moisture and softness of bakery products, improve the stability of crystal emulsions in ice cream products, reduce stickiness in candy products, and so on [32]. In addition, other uses of emulsifiers are maintaining emulsion stability in margarine, preventing fat bloom in chocolate products, and improving palatability in cake products [33].

Based on research in [34], the emulsification ability produced from an emulsifier containing a mixture of 91% MAG and 9% DAG was stable when compared to commercial emulsifiers because the emulsion capacity was 95.55% after heating, the percent stability of the emulsion only decreased a little, namely to be 90.44%. Based on research in [35], the emulsification ability produced from a mixture of 50.89% DAG and 11.68% MAG had emulsion stability of about 95.44% and an emulsion capacity of 93.63%.

The melting point of MAG and DAG is higher than their triacylglycerol forms. The difference in melting points is caused by the difference in the number of hydrogen bonds in the carboxyl bonds and the hydrophobic interactions along the hydrocarbon chains. The melting point increases as the MAG and DAG content in the fat/oil increases [36]. MAG has a faster crystal conformation compared to TAG [37]. MAG and DAG can be utilized separately (pure of MAG and pure of DAG) or simultaneously. The application of MAG as an emulsifier requires high purity because MAG has better emulsification characteristics than different acylglycerol mixtures [38].

Food emulsifiers are generally in the form of semisolids containing fatty acids such as stearic, lauric, palmitic, and oleic acids. In general, the commercially saturated MAG is MAG containing stearic acid. Saturated MAG has a high melting point but has restricted emulsifying characteristics. Nevertheless, unsaturated MAG has a modest structure but is restricted in application due to its low oxidation stability [39].

A decrease in oxidation stability can be caused by changes in the position of fatty acids in the acylglycerol structure, include MAG and DAG [40]. Partial hydrogenation can be an effective way to rectify the oxidative stability of fats/oils [41]. Zhang et al. [39] conducted a study that rivets on partial hydrogenation of corn oil to increase the MAG oxidation stability of corn oil. The oxidation stability measured based on the induction period (IP) value of the MAG from the hydrogenation of corn oil was 13.68 hours, while the IP value of the MAG of corn oil was 0.51 hours. Thus, hydrogenation increases oxidation stability. However, partial hydrogenation can lead to the formation of trans-fats, which can be harmful to health.

3. Synthesis Methods of Mono- and Diacylglycerols

3.1. Enzymatic Methods

The enzymatic synthesis method can be carried out through esterification, alcoholysis or hydrolysis, and glycerolysis. Highly stable lipases in solvents offer the potentiality of using a variety of approaches for catalyzed enzyme synthesis, such as selective alcoholysis or hydrolysis by specific lipases, glycerolysis of oils/fats, and esterification of free fatty acids with glycerol [42]. The reaction of glycerolysis by enzymatic catalysts has been extensively investigated using low temperatures (<80 °C) to generate MAG and DAG. MAG and DAG resulting from the enzymatic glycerolysis have good quality, but enzymatic glycerolysis has several shortfalls, including limited availability of enzymes, low reactant conversion factors, long reaction times, and high cost [43]. In addition, enzymatic glycerolysis has low efficiency, which is largely due to the inhomogeneous nature of oil or fat with lipophilic properties and lipase enzymes with hydrophilic characteristics when the reaction is carried out at low temperatures. It is notable for maintaining homogeneity between oil or fat and enzymes using the suitable solvent [44].

Based on research in [45], the glycerolysis between several samples of oil and fat with glycerol using lipase as a catalyst without using solvents and emulsifiers in a batch system produced 90% MAG resulting from the glycerolysis of olive oil, while the lowest yield was 30% that results from hydrogenated fat. Based on research in [3], the glycerolysis reaction of sunflower oil samples using Novozyme 435 with tert-pentanol and tert-butanol as the single solvent produced MAG in the range of 68-82%.

Based on research in [46], the enzymatic glycerolysis reaction of Lipozyme TL IM 15% using tert-butanol and iso-propanol (80/20 w/w), glycerol to oil molar ratio 3.5: 1, and solvent to oil ratio 4:1, at a temperature of 45 °C for 4 hours produced MAG about 72%. In [4], the author compared the glycerolysis between the enzyme-catalyzed reaction and the NaOH-catalyzed reaction. The reaction rate of the NaOH catalyzed was faster than the Novozym 435. Although the enzymatic approach has yielded good results; nevertheless, the high cost, reaction rate, and stability of the catalyst remain major barriers to the wide-spread use of enzymes for the commercial production of MAG and DAG.

3.2. Chemical Methods

Commercially MAG and DAG can be produced through several methods, namely: (i) direct esterification with fatty acids catalyzed by strong acids such as H_3PO_4 or H_2SO_4 at a high temperature of 90-120 °C or alkaline catalysts, (ii) glycerolysis of oil or fat which is catalyzed by homogeneous bases such as KOH or NaOH at a high temperature of 120-260 °C under an inert atmosphere, (iii) transesterification of fatty acid esters and (iv) partial or alcoholic hydrolysis [2,47].

In [48], the direct esterification using the ratio between lauric acid and glycerol of 1:1 at 112 °C using a mesoporous sulfonate catalyst 0.5% (w/w) produced MAG with a concentration of 53%. Meanwhile, under the same reaction conditions, but using Amberlyst-15 as a catalyst, it produced MAG with a concentration of 44%. The MAG produced using a mesoporous sulfonate catalyst was higher because it contains alkyl, and sulfonic acid can act as a catalyst [49]. In [50], the heterogeneous catalyst Amberlyst-15 was affected by several factors, namely the pore diameter and catalyst surface area. The use of H_2SO_4 as a homogeneous acid catalyst at a lauric acid and glycerol ratio of 1:1, a temperature of 130 °C for 6 hours, and a 5% (w/w) H_2SO_4 catalyst produced 31.05% monolaurin after going through a purification using column chromatography techniques [51].

Most of the MAG and DAG is generated by glycerolysis of TAG with excess glycerol at high temperatures in the presence of a catalyst. The addition of a catalyst to the glycerolysis reaction aims to acquire a high conversion in a relatively short time. This reaction can be performed in the existence of a base catalyst or an acid catalyst. The reaction with an alkaline catalyst is usually faster than an acid catalyst [52].

The glycerolysis reaction occurs randomly following the equilibrium to produce a certain composition of MAG, DAG, and TAG. Theoretically, the glycerolysis reaction involves 2 moles of glycerol, which will react with 1 mole of TAG and generate 3 moles of MAG. The glycerolysis reaction is used in producing MAG and DAG because it is more economical in terms of raw material prices and requires less glycerol [53]. According to [4], KOH and NaOH are catalysts that are more effective in their use in the glycerolysis process at low temperatures compared to SiO_2 and Al_2O_3.

4. Types and Concentrations of Catalysts for Chemical Glycerolysis

Chemically synthesizing MAG and DAG by glycerolysis requires a catalyst. Catalysts are substances that speed up reactions but do not react with them. The catalyst speeds up the reaction by decreasing the activation energy. The greater the concentration of catalyst and reaction temperature, the greater the reaction rate so that the product produced is also more significant [54]. Catalysts can be classified into two types, namely homogeneous catalysts and heterogeneous catalysts. The catalyst selectivity has several differences. Homogeneous catalysts are generally used for universal substrate types but are only suitable for batch reactors and cannot be used in continuous systems. In comparison, heterogeneous catalysts are more suitable for substrates or reactants that are less viscous and suitable for reactions in continuous systems [55].

In the use of a homogeneous catalyst, the catalyst is in the same phase as the reactants. The reactants and catalyst are in a single phase of liquid or gas. There are two types of homogeneous catalysts, namely homogeneous acid catalysts and homogeneous base catalysts. Homogeneous base catalysts for glycerolysis include KOH and NaOH [56]. These catalysts have advantages related to their characteristics, including high catalytic activity that only requires a short reaction time, low cost, high stability, and easy use [57]. There are also homogeneous catalysts in the form of homogeneous acid catalysts, include H_2SO_4, HCl, and H_3PO_4. However, the utilize of a homogeneous acid catalyst requires a long reaction time, causes corrosion in the reactor, and requires high temperatures [58].

In the use of heterogeneous catalysts, the catalyst and reactants are in different phases. Heterogeneous catalysts tend to be easier to separate and reuse from the reaction mixture because the phase used is different from the reaction product. The heterogeneous catalyst used is in the form of a solid phase while the reactants are liquid [59]. The most commonly used heterogeneous base catalysts are alkaline earth metal oxides compounds, such as MgO, CaO, SrO, and BaO [60].

Apart from metal oxide catalysts, there are several non-oxide catalysts that can be used, including 1-Butyl-3-Methylimidazolium Imidazolide [61]. The catalyst is also effectively used in chemical glycerolysis to produce DAG reaching about 60% at a concentration of 15%, a temperature of 80 °C for 4 hours.

Chemical catalysts are more widely used because they are easier to handle, cost less, easy to separate, and can be used in relatively low concentrations. Several types of chemical catalysts used in the glycerolysis reaction for the production of MAG and DAG are presented in Table 2.

Table 2: Several Types of Chemical Catalysts Used in the Glycerolysis Reaction for the Production of MAG and DAG.

No	Catalysts	Source of fat/oil	Reaction condition	Yield of MAG & DAG	References
1	NaOH 0.18%	Soybean oil	The molar ratio of oil:glycerol (1:2.5), 230 °C, 25 min	58% & 33%	[27]
2	NaOH 3%	Palm olein and palm stearin	The molar ratio of oil: glycerol (1:1.5), in tert-butanol, molecular sieve 12%, at 80 °C for 3 h	58.64%	[35]
3	NaOH 0.3%	Palm oil	The molar ratio of oil:glycerol (1:2), 240 °C, 60 min	58%	[62]
4	NaOH 0.45%	Soybean oil	Glycerol 4,6 g; Oil 8.8 g; in t-butanol; 50 °C, 1 h	81.76%	[4]
5	NaOH 2%	Palm stearin	The molar ratio of oil:glycerol (1:2.5), 200 °C; 20 min	65.4%	[1]
6	NaOH 3%	RBD Palm stearin	The molar ratio of oil: glycerol (1:5), in tert-butanol, molecular sieve 13%, at 90 °C for 6 h	91.00% & 9.00%	[34]
7	KOH 0.45%	Soybean oil	Glycerol 4,6 g; Oil 8.8 g; in t-butanol; catalyst 0.04 g; 50 °C, 1 h	68%	[4]
8	Amberlyst-15	RBD Palm stearin	The molar ratio of oil: glycerol (1:5), in tert-butanol, 90 °C, 9 h	16.44% & 14.49%	[34]
9	MgO	Rapeseed oil	The molar ratio of oil:glycerol (1:4), 249.85 °C, 2 h	66%	[29]
10	$Ca(OH)_2$ 1%	Sunflower oil	The molar ratio of oil:glycerol (1:4), 200 °C, 1 h	48.3% & 42.3%	[63]
11	CuO-nano+ NaOH 0.3%	Palm oil	The molar ratio of oil:glycerol (1:2), 240 °C, 40 min	71%	[62]
12	ZnO-CaO/AlO_3	Rapeseed oil	The molar ratio of oil:glycerol (1:4), 249.85 °C, 2 h	57%	[29]
13	1-butyl-3-methylimidazolium imidazolide	Soybean oil	Catalyst concentration if 15%, glycerol/TAG mole ratio was 5:1, 80 °C, 4 h	17.4% & 61.7%	[61]

The reaction mechanism of the glycerolysis catalyzed by homogeneous and heterogeneous chemical catalysts is almost the same but has some differences, especially in the active groups of cations or anions that are owned by heterogeneous catalysts. The chemical glycerolysis mechanism is described as follows. In glycerolysis using a homogeneous catalyst such as NaOH, in the early stages, the hydrogen in the glycerol molecule is abstracted by NaOH, which is a strong base to form sodium glyceroxides, which then easily form glyceroxides at high temperatures (90-240 °C). Meanwhile, the OH- anion produced from NaOH can act as a proton abstraction agent that can attract protons from the OH group on glycerol by forming surface glyceroxides. Na^+ cations also take part in the stabilization of negatively charged intermediates. In this condition, the Na^+ cation also plays a role in activating the triacylglycerol molecule (polarization of the C=O bond). The Na^+ cation further assists or facilitates the overrun of the glyceroxide anion on the positively charged carbonyl carbon present in the TAG. In a later stage, there is a nucleophilic attack on the carbonyl group of the TAG by the glyceroxides to produce MAG and the appropriate anion of 1,3 or 1,2-DAG known as diglyceroxide. The next stage is the conformation of the suitable alkyl ester (DAG) and glycerol anions (glyceroxides) by the second molecule of glycerol reacting with the adsorbed diglyceroxide. In the last stage, the alteration of TAG or DAG to MAG is carried out following the same mechanism. In contrast to homogeneous catalysts, heterogeneous catalysts that act to abstract hydrogen on the glycerol molecule are not Na^+ cations, but depending on the active groups that heterogeneous catalysts have, for example, are sulfonic or CuO groups. In addition to acting in hydrogen abstraction, this group also plays a role in polarizing the ester group (C=O) on TAG. Meanwhile, the other mechanism stages are almost the same, namely through nucleophilic attacks and ending with the conversion of TAG and DAG to MAG [64,65].

Table 2 shows that the type and concentration of the catalyst affect the results of the MAG and DAG concentrations. However, glycerolysis is also influenced by reaction conditions (temperature, the molar ratio of oil to glycerol, and reaction time). Homogeneous catalysts and heterogeneous catalysts have advantages and disadvantages. Homogeneous catalysts such as NaOH or KOH are preferred because they can readily dissolve and react with glycerol in the reactant system. Based on research in [34], the MAG produced followed by fractionation was 91.00%. The increase in MAG levels is due to differences in the melting point and the thermomechanical separation process through crystallization, namely MAG, which has a higher melting point, will be separated from DAG and TAG with lower melting points. At a fractionation temperature of 30 °C, MAG will crystallize while DAG and TAG remain dissolved in hexane and then filtered. In addition to fractionation, molecular distillation can increase monoacylglycerols with a purity of 90% [25].

Based on research in [62], using the homo-hetero system in the glycerolysis reaction resulted in almost the same triacylglycerol conversion using either NaOH or CuO-nano + NaOH catalysts. However, the product distribution was different where the MAG concentration in the use of a CuO-nano + NaOH catalyst is higher than the reaction using a NaOH catalyst. The adjunct of a small amount of NaOH (0.01% w/w) could increase the TAG conversion. In addition, the catalyst systems of CuO-nano + NaOH showed an increase in the yield of TAG to MAG conversion, reaching 90%. The use of CuOnano + NaOH catalyst resulted in a higher yield MAG than for the NaOH system; this shows that in the reaction system, CuO also acts as a catalyst.

Based on the results of the research that has been conducted, it is possible to consider three main factors that affect the glycerolysis process. These three factors are the strength of the base catalyst, the radius of the catalyst pore, and the solubility of the catalyst in the glycerol and oil system [29]. In the research of [29], using a ZnO-CaO/ AlO_3 catalyst, the results of the MAG concentration were lower than using the MgO catalyst. Based on research in [4], by comparing eight commonly used basic catalysts, namely Al_2O_3, SiO_2, MgO, Na_2CO_3, K_2CO_3, CaO, KOH, and NaOH. Only NaOH and KOH are effective in catalyzing chemical glycerolysis at low temperature (50 °C).

The homogeneous catalysts (KOH and NaOH) have high catalytic activity and result in high product yields [66]. The reason for this case remains to be investigated. This is also thought to be caused by differences in the capability to extract hydrogen from glycerol. Both KOH and NaOH have the same solubility in the tert-butanol. However, at temperatures higher than 240 °C, the $Ca(OH)_2$, MgO, and CaO catalysts are all functioning even in solvent-free systems, which exhibit easier alkoxide formation [67]. This is also supported by several studies presented in Table 1, that a high temperature of 200-250 °C produces a high MAG concentration of 77% (solvent-free system). Therefore, high temperature not only increases the solubility of oil/fat and glycerol but also helps the catalyst to extract hydrogen from glycerol to create alkoxides.

According to [5], the surface polarity of the catalyst has a key role in increasing the concentration of MAG and DAG. The glycerol concentration on the catalyst surface will be greater than the fatty acid ester for MAG formation because the high glycerol concentration will limit the forming of DAG and TAG. However, hydrophobic oils also have difficulty accessing the surface of the catalyst, thus reducing the reaction kinetics. Therefore, the catalyst must be very active, the reaction temperature used is higher, and also use a solvent to accelerate the reaction [68].

As previously explained, the glycerolysis reaction is a slow-running reaction without the addition of a catalyst. The use of various concentrations of NaOH is also expected to produce high mono- and diacylglycerols. According to [4], the catalyst concentration influences the reaction rate over a particular range, an increase in the NaOH concentration causes an increase in the reaction rate. The concentration of catalyst affects the yield of the resulting product; the higher the concentration of the catalyst in the solution, the smaller the activation energy of a reaction, so that more products will be formed [69]. However, the addition of excessive catalyst concentration can also encourage the reaction to form soap [70].

Various researches to get the type of catalyst in the glycerolysis reaction continue to develop. Recommendations that can be taken from this review are that NaOH catalysts are very effective catalysts for chemical glycerolysis reactions, but have the disadvantage of not being used repeatedly, are not environmentally friendly, and cannot be used for continuous reaction systems. Therefore, a more in-depth research is needed, especially on heterogeneous catalysts, in order to obtain a catalyst that is inexpensive, high activity, stable, able to be used repeatedly, can be used for continuous reaction systems, and environmentally friendly.

5. Conclusion

Research on the synthesis of MAG and DAG has been carried out using various enzymatic and chemical methods. Chemical catalysts have been shown to be efficient and effective catalysts, so that the chemical glycerolysis is an effective and efficient method for MAG and DAG production. However, the type and concentration of catalysts are very influential in chemical glycerolysis. Catalyst activity is affected by three main factors, namely the strength of the base catalyst, the radius of the catalyst pore, and the solubility of the catalyst in the glycerol and oil system. Homogeneous catalyst (NaOH) concentrations of 0.2-0.5% produce high yields of MAG and DAG (in the solvent systems). In the solvent-free systems, NaOH at concentrations of 3% produces high yields of MAG and DAG. Homogeneous catalysts such as NaOH and KOH are very effective for generating MAG and DAG conversions up to 91%, but they have a disadvantage, especially in that they cannot be used repeatedly. However, heterogeneous catalysts have great potential to be developed into catalysts with high activity, environmentally friendly, and can be used repeatedly.

Conflict of Interest

The authors declare no conflict of interest.

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