

Review

The Lord of the Chemical Rings: Catalytic Synthesis of Important Industrial Epoxide Compounds

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Abstract: The epoxidized group, also known as the oxirane group, can be considered as one of the most crucial rings in chemistry. Due to the high ring strain and the polarization of the C–O bond in this three-membered ring, several reactions can be carried out. One can see such a functional group as a crucial intermediate in fuels, polymers, materials, fine chemistry, etc. Literature covering the topic of epoxidation, including the catalytic aspect, is vast. No review articles have been written on the catalytic synthesis of short size, intermediate and macro-molecules to the best of our knowledge. To fill this gap, this manuscript reviews the main catalytic findings for the production of ethylene and propylene oxides, epichlorohydrin and epoxidized vegetable oil. We have selected these three epoxidized molecules because they are the most studied and produced. The following catalytic systems will be considered: homogeneous, heterogeneous and enzymatic catalysis.

Keywords: heterogeneous catalyst; enzymatic catalyst; epoxidation; epoxidized vegetable oils; epichlorohydrin; ethylene and propylene oxide



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1. Introduction

Three-membered rings are fascinating chemical functional groups because they represent an excellent compromise between stability and reactivity. The oxirane ring, consisting of two carbons and one oxygen atom, is the most representative of these three-membered rings. The synthesis of this ring is most often performed by the oxidation of unsaturated groups. Another name for this reaction is epoxidation. This reaction can be undertaken in gas, liquid or liquid–liquid systems, where a catalyst plays an important role. An overview of common epoxidation methods and routes are shown in Figure 1.

Epoxides are valuable chemical intermediates and can be used in different sectors such as surfactants, resins, fine chemicals or polymers. The interaction between carbon dioxide and epoxide [1] can produce other valuable intermediates: carbonates. According to some research groups [2,3], this reaction can contribute to valorize carbon dioxide. These carbonates are promising materials for the production of polymers such as polyurethanes [4,5].

The number of reviews dealing with epoxidation is fairly important [6–13]. De Vos et al. [6] gave an overview of heterogeneous epoxidation catalysts focusing on practical parameters and W-, V- or Mn-based catalysts. In 2007, Stephenson and Bell [7] described mechanism insights for the olefin epoxidation catalyzed by iron-porphyrin. Muzart [8] summarized the different catalytic palladium systems leading to the epoxidation of alkenes.

Hwang et al. [9] and Lin et al. [10] wrote two reviews on the production of chiral epoxides by bio-catalysis. In 2017, Danov et al. [13] studied the recent advances for the epoxidation of vegetable oils, unsaturated fatty acids, and fatty acid methyl esters, with special attention on the use of titanium silicate and polyoxometalates catalysts.

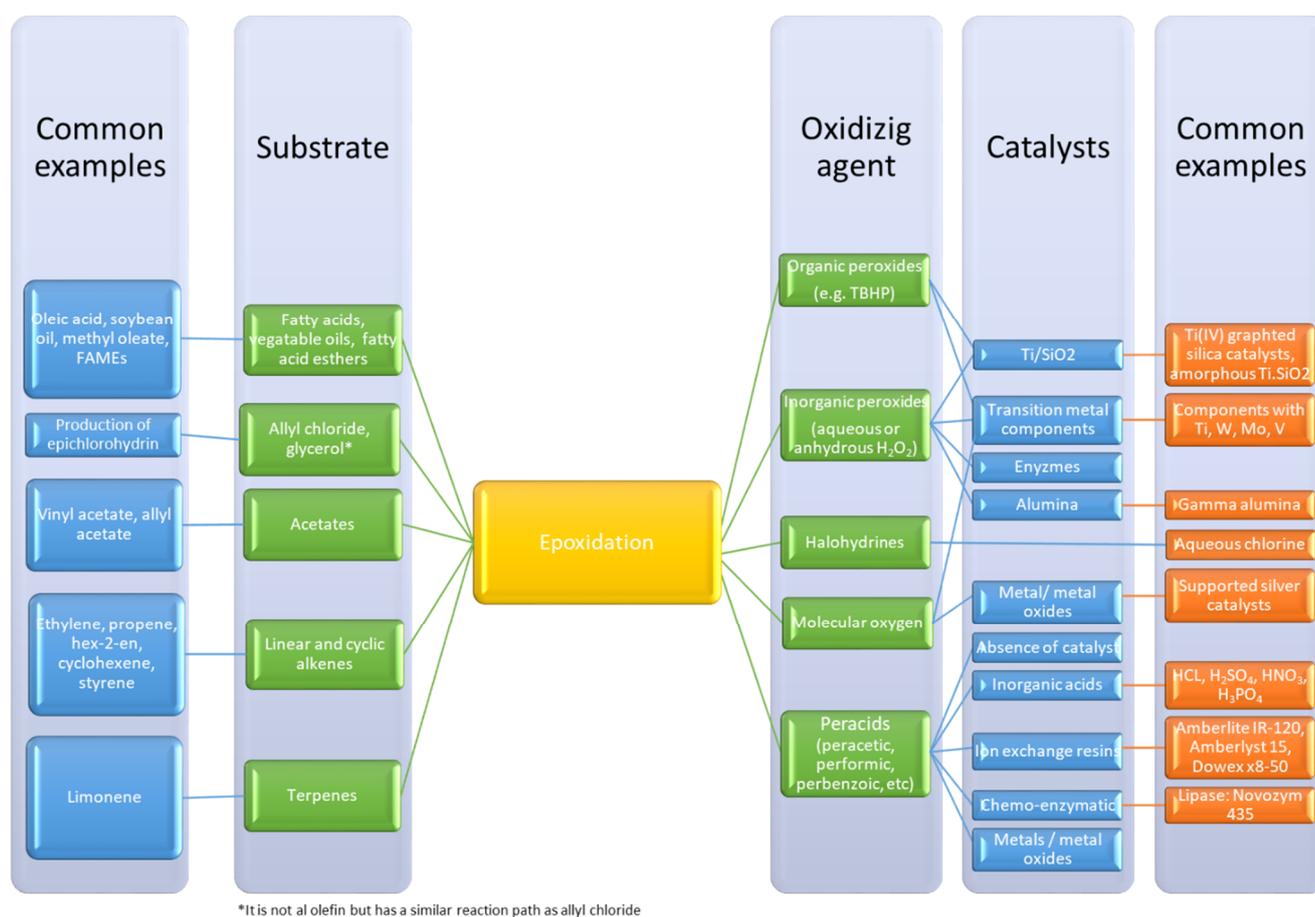


Figure 1. Overview of common epoxidation methods and routes.

To the best of our knowledge, there are no reviews concerning the synthesis of oxirane in gas, liquid, and liquid–liquid reaction systems. To fill this gap, the different catalytic ways for the synthesis of ethylene/propylene oxides, epoxidized vegetable oils and epichlorohydrin is evaluated in this review.

2. Synthesis of Ethylene and Propylene Oxide

A huge number of value-added chemicals can be produced starting from the oxidation of alkenes [14]. Ethylene is a harmful low molecular weight volatile organic molecule [15] and its oxidation is of great interest in the industrial landscape. In fact, ethylene oxide represents an important intermediate from which different types of chemicals can be obtained. Some of the best representatives are ethylene glycol, ethanolamines, detergents and epoxy resins [16–18].

The attained products in the ethylene oxidation are ethylene oxide, acetaldehyde, CO₂ and H₂O [18,19], where CO₂ is thermodynamically more stable in respect to ethylene oxide and acetaldehyde [19].

The aforementioned reaction is commonly made in fixed bed reactors using Ag/Al₂O₃ as catalyst operating at 230–270 °C and at a pressure of 1–3 MPa [20,21].

In the previous literature, different works were based on the study of this type of process and on the possible catalysts used to promote this reaction.

Ethylene is a thermally stable compound and for this reason, its oxidation at temperatures lower than 100 °C needs an active catalyst [15] finding several candidates as promising ones. Ethylene oxidation catalyzed by Ag is one of the most important chemical industry applications [22]. In Figure 2, the ethylene oxidation reaction is reported.

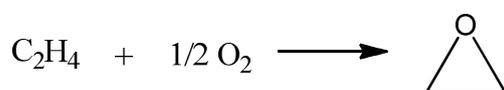


Figure 2. Synthesis of ethylene oxide.

One of the interesting aspects indicating the performance of a catalyst in this type of reaction is the selectivity [20]. It was shown that there is a correlation between selectivity itself and the conversion; in particular the selectivity decreases with the increase of the conversion [23].

In ethylene oxide production, silver is the heterogeneous catalyst which leads to a high selectivity towards the desired product [18,20]. However, this value depends on the diameter of Ag particles supported on α -Al₂O₃; more precisely the selectivity increases with the increasing of the particle diameter, as within an in-series mechanism, smaller particles lead to higher reactivity, thus lower selectivity referred to the intermediate specie (e.g., epoxide) [18].

The support (α -Al₂O₃) is characterized by low surface area and porosity [24]. The presence of impurities, such as S and Na oxides on the surface, plays the role of promoters in this reaction [20].

In particular, in the presence of unpromoted silver catalyst the selectivity towards ethylene oxide is approximately 50% while using promoters it can reach a value higher than 90% [20,25]. For this reason, the promoters are used in industrial applications, in fact the industrial catalyst is constituted by Ag particles supported on alumina with alkali compounds as promoters [22]. In order to increase the selectivity towards the desired product, also chlorine [9] or other different additives (e.g., Cs, Cl and Re) are used [18].

It was shown that adding Cs to the Ag/ α -Al₂O₃ catalysts, there was only a little increase in the selectivity, while the combined effect of the Cs and Re led to a much more positive effect [20].

Currently, supported Re/Cs/Ag/Al₂O₃ and Na/Cs-promoted supported Ag/Al₂O₃ catalysts are involved in this reaction. Furthermore, oxides of Mo and S can also promote the supported Re/Cs/Ag/Al₂O₃ in the ethylene oxide production [20].

Two different types of Ag supported on α -Al₂O₃ were tested by Christopher et al. in particular, the first one was an Ag catalyst with nanowires with mainly Ag(100) surfaces while the other one was based on Ag particles with mainly Ag(111) surfaces, since there are different activation barriers connected with the formation of the possible products. The results showed that a higher selectivity (up to 65%) was obtained in the presence of the nanowire catalysts while with Ag particle catalysts a selectivity of about 47% was achieved [18]. According to the authors, the increase in selectivity was due to a higher value of Ag(100) surfaces on nanowires with respect to the spheres, demonstrating that the selectivity was considerably influenced by the different nature of Ag surfaces and it could be controlled changing the size of Ag catalyst particles themselves [26].

Another interesting candidate for the oxidation reaction is Pt-based catalyst. In the work by Isaifan et al. [15], the ethylene oxidation on Pt nanoparticles supported on carbon and the effect of the particle size on the reaction itself was investigated. The authors showed that the Pt/C catalyst was very active in the ethylene oxidation and the reaction was widely influenced by the particle size. In particular, smaller particles showed a higher activity in comparison with the larger ones. Furthermore, an activity was visible already at lower temperatures (about 50 °C) for the smaller particles while in the case of the larger ones, a temperature of about 160 °C was needed.

Other possible candidates must be considered as alternative catalysts for this process. In the field of transition metals, Cu is very interesting. In the typically used condition for the oxidation, Cu oxidizes to CuO and the selectivity to the epoxide was of about 1%. However, it was seen that this value reached about 28% in the initial period of the reaction due to the presence of Cu₂O formed during the oxidation of Cu to CuO, but it was not stable in the reaction conditions [19,27].

It was seen by Greiner et al. that using Cu₂O, a maximum ethylene oxide selectivity was reached at 180 °C and it was equal to 21% while at higher temperature it decreased to a value of about 1.5%. On the contrary, in the presence of CuO, there was no variation of the oxidation state of Cu and the reached selectivity value was 1.5% at 240 °C. These results implied that Cu₂O represented the active phase in the oxidation reaction showing a high selectivity while when it is oxidized to CuO, which is thermodynamically more stable, the same high activity in this process was no longer observable [19].

A different catalytic system was investigated by Yang et al. [28]. In their work, the authors investigated the ethylene oxidation on microporous zeolites (ZSM-5, Beta, Y and Mordenite) and Ag/zeolites both in dry and humid atmosphere reaching a high activity in both cases.

The reaction was performed at room temperature in dry atmosphere and among the different catalytic system, Ag/ZSM-5 and Ag/Beta showed a greater stability; on the contrary, with Ag/Y and Ag/Mordenite a higher deactivation was visible.

The same tests were made in a humid atmosphere and it was seen that the presence of water influenced negatively the catalytic activities of Ag/Y and Ag/Mordenite in contrast to Ag/ZSM-5 and Ag/Beta. The active sites in the oxidation reaction were Brønsted acid sites and H₂O adsorbed on these sites caused the deactivation of the catalysts [28].

In Table 1, a summary of the different catalysts used in the oxidation reaction and the process conditions in which they were tested with the reached ethylene oxide selectivity are reported.

Table 1. Methods for the ethylene oxide synthesis.

Catalyst	Process Temperature [°C]	Ethylene Oxide Selectivity [%]	Reference
Ag/Al ₂ O ₃	230–240	50	[7,12]
Promoted- Ag/Al ₂ O ₃		>90	
Pt/C (smaller particles)	50	-	[2]
Pt/C (larger particles)	160	-	
Cu (CuO)	>240	1.5	[6]
Cu (Cu ₂ O)	180	21	
Zeolites (ZSM-5, Beta, Y, Mordenite)	25	-	[15]
Ag/zeolites			

In this context, another chemical that needs great attention is propylene. Propylene is obtained from the cracking of hydrocarbons and it can react with oxygen, in the presence of catalysts, to obtain different compounds [29]. Among these, propylene oxide is one of the most interesting since it is used in several applications and in the production of industrial materials. In particular, it counts, among its uses, the production of polyurethane foams, polyols, propylene glycols and propylene glycol ethers and by 2025, the annual request of propylene oxide will be over 20 Mt [29–31].

Different ways to produce propylene oxide exist and between them, the chlorohydrin process represents one of the most used as well as hydroperoxide process which produce tert-butyl alcohol and styrene as coproducts [32].

However, these methods show several drawbacks: corrosion of the equipment, environmental problems and the formation of many byproducts [33], in fact the coproducts of chlorohydrin process are chlorine salts, considered harmful. In the second aforementioned synthesis route, hydroperoxide is formed and it is used for the formation of propylene oxide using Mo-based homogeneous catalysts or Ti on silica as heterogeneous catalysts [30,32]. Other possible methods can be used for this purpose: the cumene process (CHP) has the

advantage that the byproduct can be transformed to cumene through dehydration and hydrogenation [29] while another one consists in the use of hydrogen peroxide to obtain peracids that are the oxidizing agents to give the propylene oxide. However, the negative aspect of this process is the low selectivity [30].

All these adverse aspects have led to the development of new ways of synthesis of propylene oxide, using an environmentally friendly oxidant [33,34].

The most interesting alternative is the process that involves the direct use of hydrogen peroxide as oxidation agent with more than 90% of selectivity using TS-1 as catalyst. Only H₂O was produced as a byproduct and for this reason it can be considered an economical and environmentally friendly process [29,30,35–37].

The scheme of the reaction of the hydrogen peroxide propene oxide (HPPO) process is reported in Figure 3.

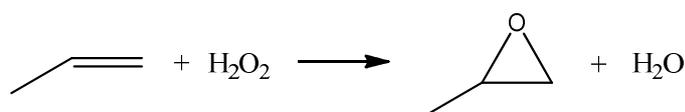


Figure 3. Synthesis of HPPO.

Among the catalysts tested in the HPPO (hydrogen peroxide propene oxide) process, the most promising was titanium silicalite-1 (TS-1) which permit to operate under mild condition [30,38]. This process permits a higher propylene conversion and propylene oxide selectivity to be reached but with the drawback of the high price of the catalyst and hydrogen peroxide [33]. A summary of the main processes for the propylene oxide synthesis is reported in Table 2.

Table 2. Main processes for the propylene oxide synthesis.

Type of Process	Process/Catalyst	Advantages/Drawbacks
Chlorohydrin process	Dehydrochlorination of chlorohydrins.	Drawback: Corrosion of the equipment, environmental problems and the formation of harmful byproducts.
Styrene monomer propene oxide process/Ter-butyl Alcohol process	Hydroperoxide from ethylbenzene/Hydroperoxide from isobutane with oxygen as oxidant. Homogeneous Mo based catalyst and heterogeneous Ti supported on silica.	Drawback: Plant complexity, problems related to the price and marketability of the process coproducts (styrene and ter-butyl alcohol).
Cumene process (CHP)	Silicon oxide catalyst with Ti in the mesoporous structure.	Advantage: Conversion of the byproduct to the initial cumene through dehydration and hydrogenation.
HPPO process	Direct use of hydrogen peroxide as oxidation agent. Titanium silicalite-1 (TS-1) as catalyst.	Advantage: Economical and environmentally friendly process with the production of only H ₂ O as a byproduct. Drawback: High price of the catalyst and hydrogen peroxide.

Different species of Ti can be found: Ti species in the framework represent the active sites in the oxidation reaction while TiO₂ species have a negative effect on the propylene oxide formation [37].

A high crystallinity structure with microporous of about 0.5 nm was observed in the TS-1 constituted by tetrahedral sites, Ti(OSi)₄, with defective sites, Ti(OSi)₃(OH).

Surface area, obtained by BET analysis is 420–450 m²g⁻¹ with pores volume of 0.18–0.26 cm³g⁻¹ [30,39].

The synthesis of TS-1 catalyst consists of several steps as follows: (i) hydrothermal crystallization of the zeolite using different silicon, titanium, templating and mineralizing agents; (ii) drying of the obtained solid at 100 °C and (iii) calcination at high temperatures (500–550 °C). The size of the produced agglomerates can be different leading to differences also in their properties.

TS-1 is used in both fixed bed reactors and continuous slurry reactors. The industrial catalyst is made by zeolite dispersed in a binder phase which is fundamental for the

mechanical properties of the catalyst itself and for the selectivity [30,40]. For example, it was demonstrated that the use of alumina instead of silica led to an increase in the production of byproducts.

Propylene oxidation catalyzed by H_2O_2 was performed in a range of 40–60 °C under pressure (20–25 bar) and using methanol as solvent. Other products could be obtained from secondary reactions that influenced the final yield. The formation of byproducts is one of the causes of the catalyst deactivation [30,35,41]. When deactivation occurs, a common way to regenerate the TS-1 catalyst is a thermal treatment in a range of 300–700 °C in the presence of air or steam or inert gases, oxidation with H_2O_2 at temperatures lower than 100 °C and extraction with different solvents at temperatures in the 140–240 °C range [30,42,43].

Many studies were focused on the propylene oxidation catalyzed by metals or metal oxides. Some of them demonstrated that these catalysts, for example Au, Ag, Cu or Cu_2O , showed catalytic activity in this type of reaction [33,34,44].

In the literature, different catalysts are proposed for the direct oxidation of propylene using molecular oxygen. A catalyst based on gold clusters on TiO_2 was very selective in the direct oxidation of propylene, but it showed the drawback of the deactivation, probably caused by sintering of gold nanoparticles, coking on the active sites and the rearrangement of TiO_2 sites [45,46].

Another promising catalyst for its high selectivity in propylene oxidation is Cu; in the last period, copper-based catalysts are becoming more important as they can be used in several applications [14]. One of the reasons why their use is increasing is their cheapness as well as the high selectivity towards the propylene oxide, as mentioned before. For example, in the literature it is reported that in the presence of Cu/SiO_2 a propylene oxide selectivity of 53% was reached for a conversion of 0.25% [47].

As for the active phase in this type of catalyst, metallic Cu^0 can be the active species in the initial times of the reaction while Cu^+ should be in the steady state, since Cu can be oxidized to Cu_2O in the oxidation conditions [48].

Ag-based catalysts were widely studied thanks to their good properties, even if the selectivity towards propylene oxide was very low [33,49]. A way to improve this value is to modify these catalysts. In particular, Zhao et al. investigated the effect of additives (Na, K and Cl) on the propylene oxidation catalyzed by silver. The authors found that a greater effect is visible for the selectivity towards the propylene oxide when Cl was used as promotor [33].

It was also found that a positive effect, in terms of activity, can be obtained by dispersing Ag on different supports alternative to Al_2O_3 or SiO_2 , such as La_2O_3 , WO_3 , MoO_3 and Y_2O_3 . The supports promote the formation of Ag(100) surfaces improving the selectivity, since this surface shows a higher selectivity towards propylene oxide [29,50–52].

3. Synthesis of Epoxidized Vegetable Oils

Vegetable oils are one of the most abundant renewable materials in the world. They all suit well as alternative feedstocks for producing chemicals and products instead of fossil-derived ones. Many of them are utilized mainly for eating and cooking purposes such as palm, soybean and olive oil, but some of the vegetable oils are non-edible, such as jatropha, karanja, rubber seed and tall oils, and can be extensively utilized for chemical modifications. Their applications are numerous—as plasticizers and stabilizers in chlorine-containing resins, as additives in lubricants, as components in thermosetting plastics, as well as in cosmetics and pharmaceutical formulations, in urethane foams and as impregnation component in woods [53].

At the moment, the largest market share of vegetable oils account for palm oil (46%)—it is cultivated extensively since it is used both in cooking as well as in the rapidly growing biofuel industry [54]. Regardless of edible or not, epoxidized vegetable oils can be used as such as lubricants or modified further into cosmetic products, surfactants, paint ingredients, resins or biopolymers. This field of research has increased drastically during the last

15 years due to the concern of global warming and the mutual intention to reduce fossil-based, CO₂-polluting production processes. Vegetable oils can be chemically modified in numerous ways, such as transesterification, epoxidation, hydroxylation, carboxylation, halogenation, hydrogenation, and oxidation. However, their epoxidation has gained a lot of attention due to the high reactivity of the epoxide group [55].

Even though epoxidation has been known for over 100 years, it has not been widely used for modification of vegetable oils until there became a market need for renewable building blocks. Before the 1990s, there was not much research related to epoxidation of vegetable oils, see Figure 4. The classical Prilezhaev epoxidation has been studied by different aspects in several groups since then.

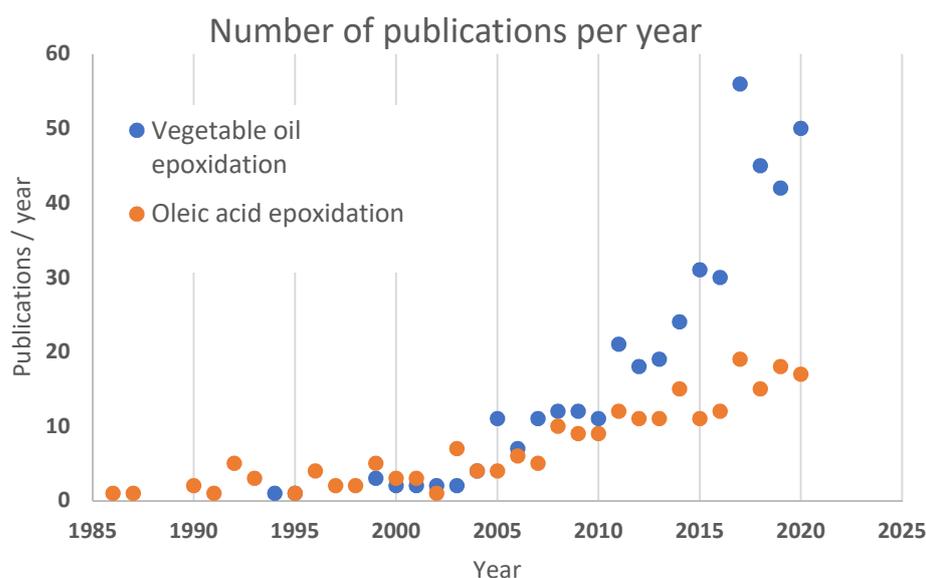


Figure 4. Number of publications per year with the search words vegetable oil epoxidation and oleic acid epoxidation, obtained from webofscience.com (some are overlapping).

There are approximately 30 review papers concerning vegetable oil epoxidation—the most recent dealing with a general overview of synthetic approaches [13], catalytic epoxidation and analysis of products [55], end-product related i.e., lubrication [56] or bio-resin [57], and process intensification-related i.e., microwave-assisted epoxidation [58]. Some reviews focus on the type of vegetable oil that is used, i.e., tall oil [59].

3.1. Classical Prilezhaev Epoxidation Method

This method for producing epoxidized vegetable oils has been known already for over 100 years. The first reported epoxidation procedure was reported by Prilezhaev in 1906 [60]. This method, which was patented already in 1946 [55] and which is still widely used, utilizes an in situ formed peroxy-carboxylic acid such as performic or peracetic acid, and the oxidant hydrogen peroxide. It works in the following way—the peracid is formed by oxidation of the carboxylic acid with a peroxide, whereafter the peracid converts the double bond into an oxirane ring (the epoxide). The most common oxidant used for the epoxidation of vegetable oils and fatty acids is hydrogen peroxide (i.e., H₂O₂) even though other peroxides can be used as well. Hydrogen peroxide is fairly inexpensive and it has a high oxidative potential. In Figure 5, the principle of Prilezhaev epoxidation is illustrated, when using oleic acid as a model compound for vegetable oil.

Table 3 categorizes the different catalytic epoxidation systems and their performances using a wide range of oil types.

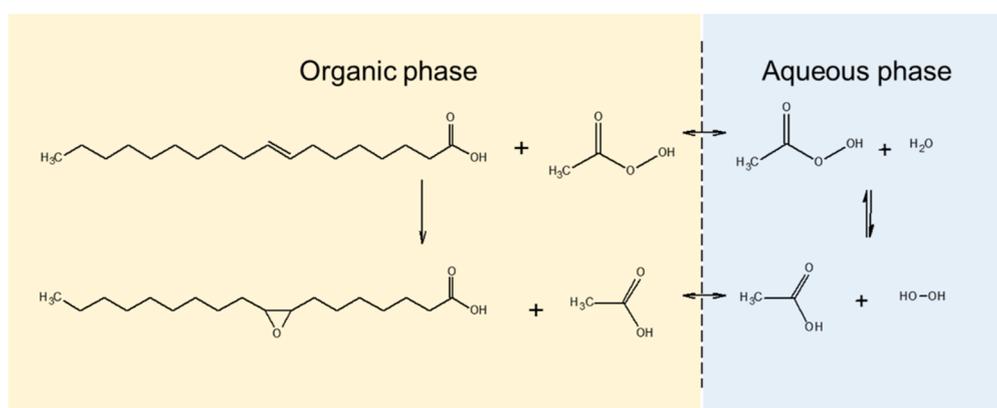


Figure 5. Epoxidation of oleic acid by the Prilezhaev method, using acetic acid.

Table 3. Overview of different types of oils, the catalytic system and their yields reported in the literature.

Catalyst	Vegetable Oil/Fatty Acid	Process Conditions		%Conversion	%RCO	Reference
		T (°C)	Time (h)			
-	Oleic acid	40; 50; 60	9; 24	62–92	16–32	Aguilera et al. [61]
	Soybean	50; 55; 60	3	49–79	45–65	Di Serio et al. [62]
	Oleic acid	50	26	80	39	Aguilera et al. [63]
	Cottonseed	30; 45; 60; 75	4–8	93.9	66–77	Dinda et al. [64]
H ₂ SO ₄	Soybean	45; 55; 65; 75	12	ns	56–81	Cai et al. [65]
	Corn	75	7.5	ns	60	Cai et al. [65]
	Sunflower	75	7.5	ns	65	Cai et al. [65]
Acetone	Jatropha	30; 50; 70; 85	3.5; 4.5; 10	35–87	41–69	Goud et al. [66]
	Soybean oil	room	18	99	high	Setien et al. [67]
	Soybean	30; 60; 75	7; 8; 9; 10	73.1–96.9	48.58–82.39	Sinadinović-Fišer et al. [68]
	Jatrofa	30; 50; 70; 85	5; 10	42–86	50–85	Goud et al. [69]
	Canola	40; 55; 65; 75	7	50–91.1	45–90	Mungroo et al. [70]
	Canola	50–60	5	71–98.5	70–99	Espinoza et al. [71]
	Rubber	60	5	92	ns	Gamage et al. [72]
	Neem	60	5	93	ns	Gamage et al. [72]
	Mee	60	5	93	ns	Gamage et al. [72]
	Anion Exchange resin (AIER)	Sucrose linseedate	55–65	ns	99.9	88
Sucrose safflowerate		55–65	ns	99.8	90	Pan et al. [73]
Sucrose soyate		55–65	ns	99.6	93	Pan et al. [73]
Sucrose soyate		55–65	ns	99.4	91	Pan et al. [73]
Soybean		50; 65; 75; 80	8–10	65–98.7	62–87.7	Jankovic et al. [74]
Soybean		45; 55	3	96–98	60–80	Di Serio et al. [62]
Tall oil fatty acids		60	6	81	44	Vanags et al. [75]
Oleic acid		50	6	97	78	Aguilera et al. [63]
Cottonseed		40	5	73	72	Aguilera et al. [63]
Tall oil fatty acids		50	6	88	73	Aguilera et al. [76]
Chemo-enzymatic	Soybean, sunflower, linseed, rapeseed	Room temperature	16	88–99	88–96	Rüsch et al. [77]
	Soybean	50	24	48–98.9	45–92	Rüsch et al. [77]
	Sapindus mukurossi	30; 35; 40; 45	10	ns	44–88	Vlček et al. [78]
	Oleic acid	50	24	ns	86–88	Törnvall et al. [80]
	Tall oil fatty acids	40	7	51–80	45–67	Kirpluks et al. [81]
Metal/metal oxides	Soybean	Room temperature	1–2	16–92	15–95	Gerbace et al. [82]
	Fatty acid mixture	30	2	41–92	ns	Cai et al. [83]
	Rapeseed	90	4	26–44	ns	Dworakowska et al. [84]
	Castor	Ns	6	94	84	Parada et al. [85]
	Methyl Oleate (aluminium oxide)	74	25	90	73	Perez Sena et al. [86]
	Sunflower oil (CuO/gamma-Al ₂ O ₃)	100	6	99	78	Scotti et al. [87]

ns = not specified, RCO = relative conversion to oxirane.

As previously described, the Prilezhaev reaction consists in two reactions, the perhydrolysis and the epoxidation, being the perhydrolysis the rate-limiting step. Overall, studies have shown that strong inorganic acids are good catalysts for the perhydrolysis reaction. Dinda et al. [64] have investigated the suitability of various inorganic acids as catalysts, i.e., HCl, H₂SO₄, HNO₃ and H₃PO₄, for the epoxidation of cottonseed oil with peracetic and performic acid generated in situ and concluded that sulfuric acid was the most effective catalyst. In fact, H₂SO₄ is the most common catalyst used in this synthesis. On the other hand, strong inorganic acids are highly corrosive and difficult to separate once the synthesis is completed. Furthermore, the presence of strong mineral acids in the

epoxidation leads to ring-opening reactions which reduce the selectivity [88]. In general, heterogeneous catalysts are advantageous in terms of reusability and ease of separation when compared to its homogeneous counterparts. Among the solid catalysts for the epoxidation of vegetable oils, acidic ion exchange resins (AIER), lipase-based enzymes and metallic and metal-based catalysts can be used.

Using formic acid has been long known to be much faster than longer-chained carboxylic acids, and yields are also high, but there are large safety risks using formic acid due to the highly exothermic nature of the reaction [89]. Even with acetic acid, some precaution is needed. There have been several publications recently relating to the thermal safety of the vegetable epoxidation process [90–94], discussing in detail the thermal risks present in the Prilezhaev system and providing a kinetic model under adiabatic conditions to estimate for instance, the important time-to-maximum rate parameter. The safety issues were also studied and modeled by the Italian group of Di Serio, who have epoxidized soybean oil with performic acid and both sulphuric acid and solid acid catalysts [95]. The group has additionally studied the development of continuous epoxidation processes [96].

Previous reviews on the subject point out that metal-based catalysts are usually applied for epoxidation with H_2O_2 and produce lower conversions and yields compared to acidic ion exchange resins (AIERs) and enzymes [97]. Leveneur [98] studied the use of several highly complex zeolite catalysts for enhancing the perhydrolysis of peracetic and perpropionic acid with hydrogen peroxide and concluded that aluminosilicate materials were less beneficial than ion exchange resins in this reaction because aluminosilicates promoted the undesired decomposition of H_2O_2 .

Epoxidation with AIER has been conducted for a wide variety of plant oils and operating conditions, and it is the most reported method. Its use affords easier catalyst separation and reduces undesired ring-opening reactions [68,70]. Ion exchange resins are rather active and inexpensive catalysts available for this process. An acidic ion exchange resin is an acid in solid form, which is insoluble in water. These resins have a network structure typically conformed by styrene-divinylbenzene, functionalized with acidic sulfonic groups. The ionic nature of the structure gives the resin the capacity to hydrate and retain water or polar/hydrophilic components into its network. A variety of ion exchange resins are commercially available with different matrix compositions, pore sizes, crosslinking percentages and particle sizes.

The first ones who made a thorough research campaign on the kinetics and modeling of Prilezhaev epoxidation with ion exchange resins were the group of Petrović [68,99] in the early 2000s. Using acetic acid, soybean oil, and AIER Amberlite 120H, Petrovic created a kinetic model that takes into consideration two side reactions of the epoxy-ring opening involving the formation of hydroxy acetate and hydroxyl groups as well as the reactions of the formation of the peracid and epoxy groups, and the catalytic perhydrolysis reaction was characterized by adsorption of only acetic acid and peracetic acid on the active catalyst sites, whereas the irreversible surface reaction was the overall rate-determining step. The benefit of the porous structure of the solid catalyst was found to be the minimization of undesired side reactions of ring-opening and improvement of selectivity, compared to the classical sulphuric acid catalyzed way. The Amberlite 120H has more or less become the classical heterogeneous catalyst used in the vegetable oil and free fatty acid epoxidation studies.

Amberlite 120H was also used by a group of Campanella and Baltanas, who investigated the bi-phasic modeling of soybean oil epoxidation as well as ring-opening reactions [100], by the group of Goud, who studied Amberlite 12H-catalyzed epoxidation of various oils including cottonseed [64], karanja [101], jatropha [69]. In these studies, it was explored how the process parameters such as temperature, molar ratios, and type of carboxylic acid influence on the conversion and yield.

Numerous kinetic models have been proposed by Jankovic [68,102] and Goud [70,103], which can be classified mainly into pseudo-homogeneous and pseudo-two-phase models. However, these models are not well-predicted oils that have a higher degree of unsaturation. i.e., that are rich in polyunsaturated fatty acids such as linoleic acid. This consideration

was well tackled by Pilla et al. [104], who developed a pseudo-two-phase model that captures the variation in reactivity of chemical groups based on their position, using the epoxidation kinetics of high-linolenic perilla oil (containing >65 wt.% linolenic acid). Based on experimental observations, it is assumed that the reactivity of double bonds at the 9th and 12th positions are the same, while that of the double bond at the 15th position is different.

Generally, the resin catalyst enhances the perhydrolysis reaction, i.e., speeding up the in situ formation of the percarboxylic acid in the aqueous phase but does not enhance the actual epoxidation rate. The bottleneck here is the mass transfer of the per compound between the aqueous and oil phase. To overcome this, the stirring velocity can be increased but it has a limited enhancement. In another approach, the group of Salmi has studied the influence of using microwave irradiation and ultrasound [61,63]. It was found that microwave irradiation can in fact enhance significantly the oleic acid epoxidation yield, if no catalyst is used. However when using Amberlite 120H, the benefit was overshadowed by the fast kinetics obtained by the solid catalyst. In another attempt to enhance the mass transfer in the epoxidation of oleic acid with Amberlite IR-120, Aguilera et al. [105] have applied ultrasound irradiation to the three-phase system. However, the ultrasound irradiation produced deactivation of the catalyst, and the experiments under silent conditions resulted in higher yields of epoxide. Even though the most widely studied solid catalyst has been the AIER Amberlite 120H, there exist other suitable catalysts as well for the reaction system. Importantly, the main task of the catalyst is to enhance the perhydrolysis reaction in the aqueous phase, and not take part in reactions in the oil phase, since the products are sensitive for ring-opening at highly acidic environments. Therefore, a suitable catalyst should preferably not allow the epoxide to be in contact with the acid sites. In this sense, a resin catalyst suits well since it is porous and the bulky organic oil molecules are not entering the pore channels, thus limiting ring-opening reactions.

Salmi et al. have performed a thorough catalyst screening for epoxidation of oleic acid using several different solid acid catalysts, such as Amberlite IR-120, Amberlyst 15, Smopex, Dowex 50 × 8–100, Dowex 50 × 8–50, Dowex 50 × 2–100 and Nafion. They found out that the best performing acid catalyst in terms of oxirane yield after 6 h of reaction time at 50 °C was obtained with Dowex 50 × 8–50 (87.9%, conversion, 68% relative conversion to oxirane, RCO), followed by Dowex 50 × 8–50 (78% conversion, 67.5% RCO) and Amberlite IR-120 (86% conversion, 59.9% RCO). However, with a longer reaction time, the values would have been higher, noted from the kinetic curves. An explanation for the highest selectivity with Dowex 50 × 8–50 was explained by that it has high capacity, small particle size and a degree of crosslinking that is high enough to reduce the probability of the epoxide making contact with the internal acid sites and triggering the ring-opening reactions. Another study by Kuranska et al. [88], consisted of the epoxidation of used cooking oil and a variety of Dowex AIERs were screened. No significant effect of the size, as well as the porosity of the catalysts on the properties of the final yield, was observed by them. However, a more economically viable process was studied by using waste cooking oil and Amberlite IR-120 as a cheaper catalyst and the catalyst proved to be reusable for several cycles.

To suppress the ring-opening, using a solvent such as toluene works efficiently [99]. However, researchers have recently been avoiding using solvent for environmental reasons. Therefore, nowadays, many researchers use either pure oil or fatty acid solutions, or they prefer to esterify the reactants to methyl esters which protect the formed epoxy groups from ring-opening and provides lower viscosity epoxidized mixtures that are easier to operate.

There were also studies on the kinetics by the Argentinian group of Campanella [100, 106,107], who used a different, titania-based solid porous catalyst for the epoxidation of soybean oil and soybean methyl esters in the presence of tert-butyl alcohol. The influence of the temperature and the hydrogen peroxide-to-double bond molar ratio on the reaction were studied. An excess of hydrogen peroxide was not shown to be necessary to increase the reaction rate since the highest yields of epoxide were obtained with a 1:1 H₂O₂ : substrate molar ratio. Under the experimental conditions employed in this work, no

degradation of the oxirane ring was observed. Subsequently, Campanella et al. have dedicated several studies that focus on the study of the ring opening reactions that are associated with the Prilezhaev epoxidation [100,106,107]. Cai et al. [108] have studied in-depth the ring-opening reactions for the system: epoxidation of cottonseed oil by peracetic acid produced in situ. They demonstrated that ring-opening by acetic and peracetic acids is faster than by water and hydrogen peroxide.

Drawbacks with the classical Prilezhaev method

Hydrogen peroxide is considered non-toxic because it decomposes into water and oxygen. However, hydrogen peroxide is a polar molecule and hence it is not miscible with non-polar oily components. This hinders the epoxidation process since mass transfer limitations might appear and adequate solvents are usually required. Typical catalysts used for this method are metallic components, enzymes and alumina [109]. Moreover, these catalysts can trigger hydrogen peroxide decomposition [110–112] or in the case of the enzymes, they can deactivate at high temperatures or high concentrations of H₂O₂ [113]. For organic peroxides, moreover, transition state metal catalysts are commonly used [114,115]. Aqueous chlorine is the preferred reactant for epoxidation with halohydrines and solvents are typically required for non-polar olefins. This process is highly toxic for the environment and it is best to avoid [116]

One drawback with the system is that it operates in several phases and therefore, the reaction velocity is limited by a slow mass transfer of the reactive species between the phases. Another drawback is that it works best with high-oleic acid (C18:1) vegetable oils, whereas the epoxidation of linoleic acid groups and higher unsaturation fatty acids, may sterically hinder the reaction [103].

Alternative/new epoxidation methods/approaches

An essential drawback of the Prilezhaev method is the complex reaction system. The risks for temperature runaway in the formation of the percarboxylic acids are rather high. Additionally, the acidity present in the system from the reaction carrier and the catalyst are an impediment when it comes to product separation, and it promotes ring opening. Utilizing an AIER catalyst also has its own challenges—disadvantages are that resin degrades chemically and physically and needs to be changed after 6–8 runs. At the end of the reaction, the employed organic acid is not recovered, and, in the case of formic acid, it is degraded to CO₂ and H₂ and cleaner and more selective oxidation processes than those based on the peroxy-acids are desirable [117].

Alternative routes are reported to be more selective and environmentally friendly. The oxidant can be changed to a less unstable type than the peracids, or the catalyst can be changed to another one, which operates at lower temperatures and causes fewer risks for thermal instability. Some recent vegetable oil epoxidation methods are reported below.

Homogeneous catalysis

The classical Prilezhaev epoxidation oleic acid was epoxidized with high yield using homogeneous catalysts such as sulphuric acid. Thorough studies of various vegetable oils have been performed by the group of Goud, where sulphuric acid was the catalyst, such as cotton oil [64], mahua [118], as waste cooking oil [119].

Using strong mineral acids is nowadays not desirable and alternatives have been developed using oxygen instead of hydrogen peroxide. The presence of benzaldehyde and a cobalt (II) tetraphenylporphyrin compound enabled organic peracids to be synthesized from aldehydes and oxygen, instead of hydrogen peroxide [120]. Later, epoxidation of oleic acid catalyzed by peroxy phosphotungstate in a two-phase system was reported [121].

3.2. Other Catalytic Systems

Due to the exothermal nature of the Prilezhaev epoxidation, new types of epoxidation routes have been investigated. The use of γ -alumina have recently been reported to be an efficient epoxidation catalyst, giving high epoxide yield when using a solvent like toluene [122] or acetonitrile [123], and hydrogen peroxide.

A continuation of this was undertaken by Perez-Sena et al. [86] performed the direct epoxidation with hydrogen peroxide and solid γ -alumina catalyst. This group studied the kinetics of the direct epoxidation of methyl-oleate by hydrogen peroxide and aluminum oxide and they found that a semi-batch addition of hydrogen peroxide decreases the side reaction of hydrogen peroxide decomposition. However, long reaction times were required.

Mesoporous niobium silicates ($\text{Nb}_2\text{O}_5\text{-SiO}_2$) have been found to be an effective catalyst for cyclooctene and cyclohexene epoxidation [124]. Therefore, the group of Di Serio performed epoxidation with several different niobium catalysts, finding that the catalyst with the lowest amount of niobium was the most active. However, the selectivity trend was the opposite. This is connected to the Brønsted acid sites which can catalyze the reaction of the epoxide ring with water, forming a diol group [117].

Nanotube-structured Ti-containing mesoporous has been successfully used in the epoxidation of methyl oleate with a high yield of 98%, using tert-butyl hydroperoxide (TBHP; 5.0 M in decane) as oxidant and a relatively large amount of dichloromethane as solvent. The catalyst showed excellent stability [125]. Another titania using a study performed epoxidation of methyl oleate in a TiO_2 coated-wall capillary microreactor with H_2O_2 , EDTA and formic acid, and no solvent, and achieved with a continuous operation 23 times higher reaction rate of epoxide production than with a batch reactor. However, the catalyst layer was slowly peeled off, reducing the performance [126].

Metal organic frameworks have attracted considerable attention since they possess a unique combination of properties such as high surface area, crystalline open structures, tunable pore size, variety of metal and functionality and have already shown success in the epoxidation of olefins and oxidation of alcohols with hydrogen peroxide [13]. However, MOF-related oil epoxidation research seems still to be low in quantity—one reference was found from 2017, where $\text{MoO}_2(\text{acac})_2$ containing catalytic system was used for Epoxidation of soybean oil [127].

3.3. Enzymatic Epoxidation

The enzymatic method has gained some popularity since it is considered a green method and a favorable one as it suppresses undesirable ring-opening of the epoxide and can lead to high selectivity. Moreover, in contrast to chemical epoxidation, with enzymes one can produce diepoxides and even triepoxides [128]. Usually, polyunsaturated fatty acids do not form di- or triepoxides with chemo-catalysed systems due to sterical hindrance. The increase of epoxy groups is challenging, as there exists the possibility of steric hindrance and electronic effects from the bulkier glycerol center, the triglyceride backbone, influencing the reactivity of double bonds located at varying positions in fatty acids [129].

In the chemo-enzymatic process, the reaction process is simplified since there is no need for a carboxylic acid as an oxygen carrier. The reactions are conformed only by the oil substrate, hydrogen peroxide and the enzymatic catalyst, which commonly is of the type called Lipase. This means that the acidic reagents are not present, and the process becomes more environmentally friendly. However, some authors report that the use of butyric, lauric or stearic acid as an oxygen carrier enhances the reaction yield [130–132].

Ever since the enzyme catalysts have been immobilized, they have shown higher stability and reusability [133]. However, the main drawbacks for the chemo-enzymatic method are the fact that low stability of the enzyme and the price of the immobilized enzyme become an impediment for the study, development and utilization of the process. Some enzymatic catalysts tend to deactivate during the course of the reaction or are susceptible to degradation at high temperatures or high concentrations of hydrogen peroxide [134].

3.4. Oxone Epoxidation

A lucrative option would be to perform high yield epoxidation at room temperature and without the use of peroxides and acids, to avoid heating cost and acidic waste. One

possibility is to utilize a peroxymonosulfate (PMS, KHSO_5 , tradenames Oxone or Caroat) in combination with a ketone such as acetone. Its active constituent is the potassium salt of Caro's acid, peroxymonosulfate [135]. The oxidation potential of this compound has recently gained attention and in fact a review paper on the activation of PMS is at this moment the most cited paper in *Chemical Engineering Journal* since 2018 (762 citations on March 2021) [136]. This method generates in situ dioxiranes to epoxidize alkenes at high yield and at low (room) temperature. The active component here, the dioxirane, is one of a merely new class of oxidants that have been gaining attention due to their excellent, high selective oxidation as well as epoxidation capabilities at room temperature and mild reaction conditions [129,137]. The PMS-ketone chemical system allows the oil to be solubilized in the oxidant milieu due to the present solvent acetone, which also serves as the catalyst, see Figure 5. This catalytic cycle is a modification of the Shi epoxidation (Figure 6) [138]. Using this catalytic system, the oil epoxidation synthesis works well and high yields are reported (up to 98%) [102].

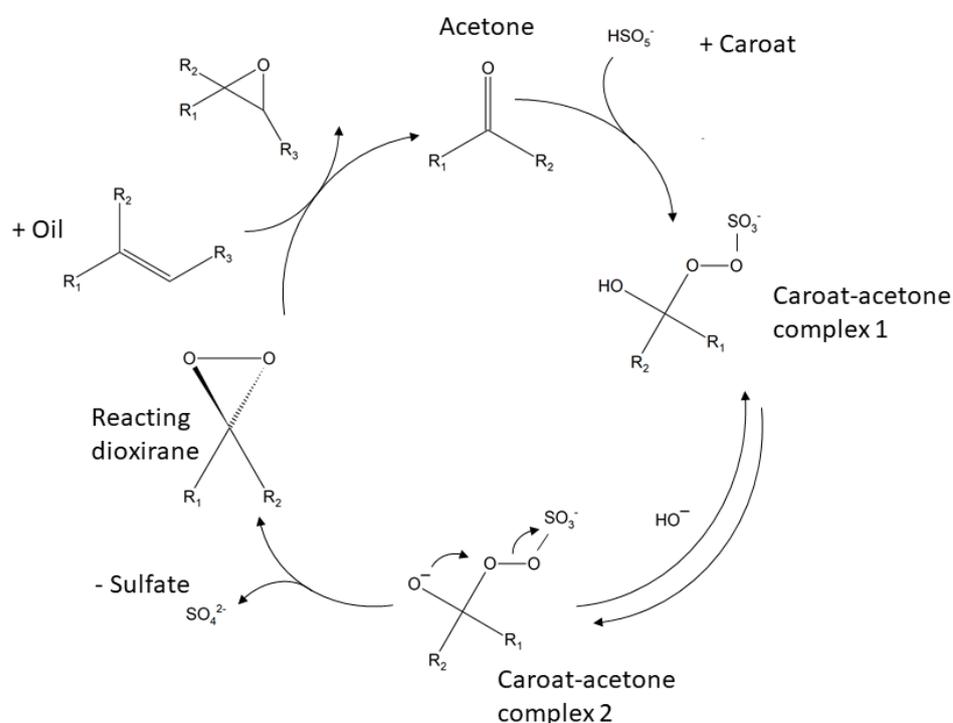


Figure 6. A redrawn illustration of the Caroat-acetone reaction cycle proposed by Shu and Shi (2000) [138].

However, there are some drawbacks with epoxidizing with Oxone/Caroat, such as a long synthesis time since the oxidant needs to be added slowly, and the oxidant is prone to self-decompose if the concentration of dimethyldioxirane (DMDO) in the medium is too high [139,140]. The decomposition of DMDO is a second-order reaction that is very sensitive to pH, ionic strength and impurities. Additionally, The pH level needs to be carefully adjusted for instance by adding a base (NaOH or KOH) slowly or alternatively using a large amount of buffer solution. The recovery of the product also requires several steps such as washing and drying. Recently, a research performed by Setien et. al [67] compared the product quality between oil epoxides synthesized by the Oxone method and acetic acid/hydrogen peroxide method. They also undertook an environmental sustainability assessment using green chemistry principles evaluating the safety and efficiency aspects. They reported that the peracid method (also known as Prilezhaev) is atom economic and generates less waste. However, the dioxirane method offers better occupational safety and requires less energy, demonstrating the tradeoffs involved depending on which pathway is selected.

4. Synthesis of Epichlorohydrin

4.1. Synthesis of Epichlorohydrin from Propene

As an important intermediate used in the medical and chemical fields, the traditional industrial production technology had many drawbacks such as high energy consumption, environmental pollution and low production yield. High-temperature chlorination of propene using chlorine gas and calcium hydroxide was firstly proposed by Shell Development Company, Houston, Texas, USA in 1948. As shown in Figure 7, the reaction mechanism of epichlorohydrin (ECH) synthesis from propene has three steps.

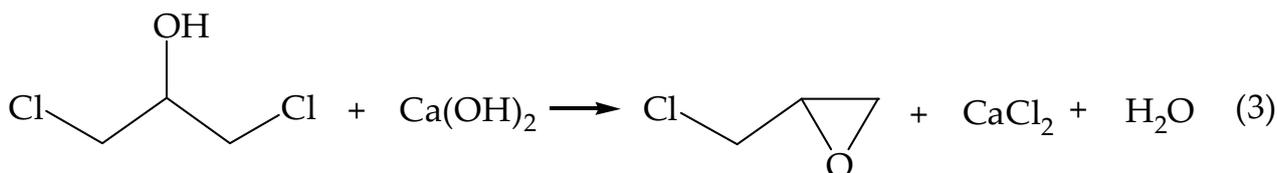
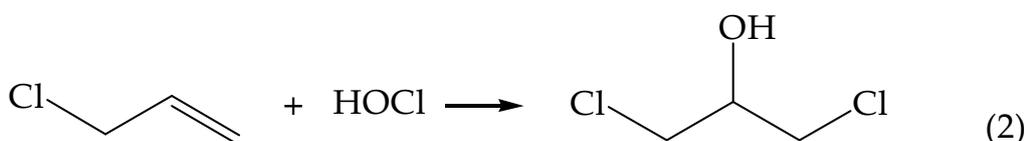
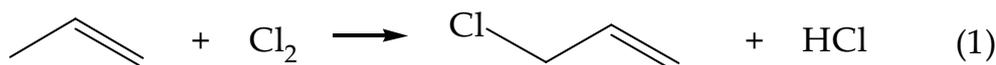


Figure 7. Reaction mechanism of epichlorohydrin synthesis from propene.

This technology of producing ECH from propene is mature, stabilized, continuous and automatic. However, the synthesis method also has many disadvantages, including numerous byproducts, high energy consumption, low conversion rate and environmental pollution.

4.2. Synthesis of Epichlorohydrin from Allylchloride

In recent years, eco-friendly ways to produce ECH are becoming more attractive among many researchers and industrials. Hydrogen peroxide is a relatively cheap, environmentally friendly oxidant with an atom efficiency of 47%. Direct epoxidation of allylchloride with hydrogen peroxide is an ideal method with no byproducts and eco-friendly. As displayed in Figure 8, epichlorohydrin synthesis by one-step epoxidation of allylchloride is a good process. A summary of different catalyst systems is shown in Table 4.

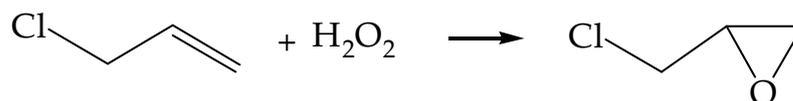


Figure 8. Reaction mechanism of epichlorohydrin synthesis from allylchloride.

Among these catalysts, Ti-MWW was proved to be a promising catalyst for the efficient synthesis of ECH. It shows high catalytic activity and product selectivity. Wang et al. [140] investigated the catalytic properties of Ti-MWW for the epoxidation of allyl chloride with H_2O_2 . When the reaction conditions were: 0.1 g Ti-MWW (Si/Ti = 37), 10 mmol allyl chloride, 10 mmol H_2O_2 (30%), 5mL CH_3COCH_3 , a high conversion rate (96.1%) was achieved after 2 h of reaction at 60 °C, and the selectivity was 99.9% for H_2O_2 . Moreover, during the allyl chloride epoxidation, Ti-MWW exhibited high stability, maintaining a high

conversion rate of allyl chloride and selectivity after six regeneration cycles and leaching the Ti-active species was found to be less than 5%.

Table 4. Summary of catalyst systems for one-step synthesis of epichlorohydrin.

No.	Substrate	Oxidant	Catalyst	Solvent	Reaction Conditions	Conversion/Selectivity with Respect to the Hydrogen Peroxide	Ref.
1	Allyl chloride	Percarboxylic acid (-COOOH)(perpropionic acid)	H ₂ SO ₄	Inert chlorine-based hydrocarbon solvents	345 K, 1.01 bar, cascade reaction solvent: 1,1,2,2-tetrachloroethane: 1,2-dichloropropane (52:13)	-/100%	[141]
2	Allyl chloride	Alkyd hydrogen peroxide (ROOH)	Ti(IV)/SiO ₂ (MgO)		80 °C–100 °C, n(C ₃ H ₅ Cl):n(ROOH) = 5:1–10:1	Above 80%/-	[142]
3	Allyl chloride	Hydrogen peroxide (H ₂ O ₂)	chlorine-based quaternary ammonium salt	Benzene-water solvents (ph = 2)	60 °C, 2.5 h, n(C ₃ H ₅ Cl):n(H ₂ O ₂) (55:12)	96%/80%	[143]
4	Allyl chloride	Hydrogen peroxide (H ₂ O ₂)	TiO ₂ 2.8 wt%, SiO ₂ /TiO ₂ molar ratio 46	Methanol	45 °C, 0.5 h,	98%/92%	[144]
5	Allyl chloride	Hydrogen peroxide (H ₂ O ₂)	titanium silicalite	Methanol	25 °C, 2.5 h n(Methanol):n(C ₃ H ₅ Cl):n(H ₂ O ₂) = 15.6:2:1	89%/99%	[145]
6	Allyl chloride	Hydrogen peroxide (H ₂ O ₂)	Ti-MWW	aprotic solvent (acetone, acetonitrile)	60 °C, 2 h	96.1%/99.9%	[140]
7	Allyl chloride	Hydrogen peroxide (H ₂ O ₂)	Ti-ASM-5	Methanol	50 °C, 1 h n(C ₃ H ₅ Cl):n(H ₂ O ₂) = 3:1	100%/-	[146]
8	Allyl chloride	Hydrogen peroxide (H ₂ O ₂)	Titanium silicate-1 (TS-1)	No information	No information	99.5%/-	[147]

4.3. Synthesis of Epichlorohydrin from Glycerol

As the main byproduct of biodiesel production, glycerol is an alternative material for epichlorohydrin synthesis. The synthesis of epichlorohydrin (ECH) from glycerol consists of two steps: chlorination with HCl in hexanoic acid solution and then epoxidation with Ca(OH)₂ (or NaOH), as displayed in Figure 9.

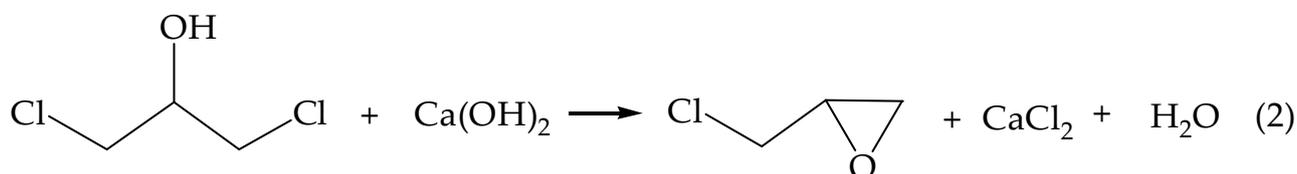
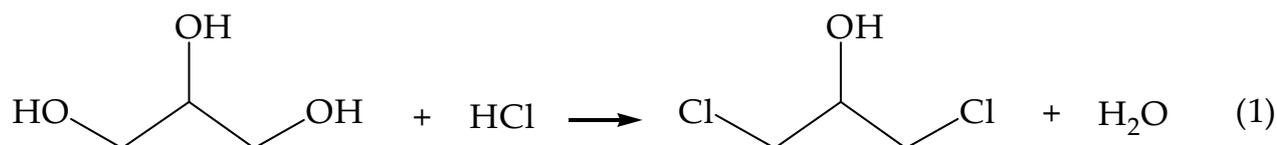


Figure 9. Reaction mechanism of epichlorohydrin synthesis from glycerol.

In the first step, the chlorination of glycerol with hydrogen chloride and catalysts (Table 5) is undertaken to obtain dichlorohydrin and 3-monochloro-1,2-propanediol at a suitable temperature. In the second step, dichlorohydrin (DCH) is epoxidized using an alkaline solution, which was prepared with calcium hydroxide/sodium hydroxide.

Table 5. Summary of catalyst systems for two-step synthesis of epichlorohydrin.

Item	Substrate	Chlorination Agent	Chlorination Solvent	Chlorination Catalyst	Reaction Conditions	Yield/conVersion	Deactivation	Ref.
Step-1 Chlorination	Glycerol	Hydrochloric gas	Dibutyl ether, dichloroethane, dichloropropene or chlorobenzene	Organic acids (anhydrous acetic acid)	100 °C	No information	No information	[148]
	Glycerol	Hydrochloric gas	Water	Organic acids (hexanedioic acid)	110 °C, 3 h	85%/97%	No information	[149]
	Glycerol	Hydrochloric gas	Water	Organic acids (hexanedioic acid)	120 °C, 20 h	–/95%	No information	[150]
	Glycerol	Hydrochloric gas	water	n(hexanedioic acid):n(acetic anhydride) = 3:2	115 °C, 5 h	69.5%/99.7%	No information	[151]
Step 2 Epoxidation	Dichlorohydrin	Super base catalyst (Ca(NO ₃) ₂ /K ₂ CO ₃ /(HOCH ₂ CH ₂) ₃ N/γ-Al ₂ O ₃)			353 K, 4 h	96.5%/–	No information	[148]
	Dichlorohydrin	No information			30 °C,	91.79%/–	No information	[150]
	Dichlorohydrin	No information			40 °C	99.77%/69.7%	No information	[152]
	Dichlorohydrin	Mg, Ca, Ba nitrates and chlorides/γ-Al ₂ O ₃			150 °C–330 °C	98.4%/90%	No information	[153]
	Dichlorohydrin	halohydrin dehalogenase			40 °C, 25–70 min	95.2%/–	retained >90% of the initial conversion after 50 cycles of reaction	[154]
	Dichlorohydrin	No information			323.2 K, 20 min	50%/97%	No information	[155]

Zhao et al.'s study demonstrated that hexanedioic acid has the most efficient catalytic effect on the chlorination of glycerol among glacial acetic acid, oxalic acid, succinic acid, hexanedioic acid and octanoic acid [149].

In a previous study, Ouyang et al. prepared DCH using glycerol and hydrogen chloride with hexanedioic acid as a catalyst, and synthesized ECH from DCH with sodium hydroxide (1.9 mol/L) [150]. The ECH yield was 91.79% at 120 °C, with a flow rate of hydrogen chloride gas of 326.4 mL/min, a chlorination time of 20 h and a mole ratio of catalyst and glycerol of 16:100.

Meanwhile, the catalytic system for the chlorination of glycerol was also explored. Zhang et al.'s study showed that the yield of DCH could be increased to 5.47% and 2.8% with the composite catalyst system of hexanedioic acid-acetonitrile and hexanedioic acid-acetic anhydride, respectively, and compared to the catalytic system of hexanedioic acid [152]. The composite catalyst system of hexanedioic acid-acetic anhydride was chosen to be the catalyst, and the yield of DCH was 69.5% and the conversion of glycerol was 99.77%.

The intermediate, DCH, could be directly produced from glycerol and hydrogen chloride without chlorine. Therefore, this type of reaction system has many advantages such as more resources, shorter technical processes, less investment, less consumption of water and energy, safer operation, fewer byproducts containing chloride, and is more environmentally friendly.

For the reaction system with hydrogen chloride liquid, during the chlorination step, the high content of moisture brought by the liquid of hydrochloric acid into the reaction system could lead to a lower yield of dichlorohydrin through decelerating the reaction rate, prolonging the reaction time, and promoting the production of byproducts. Therefore, dehydration is the most critical procedure in this chlorination system. The reaction system with hydrogen chloride gas results in a high yield of dichlorohydrin with the advantages of increasing reaction rate and reducing reaction time. Also, hydrogen chloride gas could be

produced by the reaction of sodium chloride with concentrated sulfuric acid or the reaction of phosphorus trichloride with hydrochloric acid.

The kinetics of glycerol hydrochlorination with gaseous HCl was studied in detail by Araujo et al. [156], using acetic acid as catalyst. They found that the production rate equation contains the catalyst concentration both in the nominator and denominator, evidencing that the catalyst also plays a somewhat retarding role in the production of 1,3-DCP. Based on this observation, a catalyst modulus was developed and successfully tested [156].

Moreover, the yield of ECH will be low once the reaction system contains an excess of alkaline solution leading to the accelerated hydrolysis of ECH to glycerol. Thus, ECH should be collected immediately to avoid the formation of byproducts. Moreover, the epoxidation of DCH and the yield of ECH can be easily affected by factors including mole ratio, temperature, reaction time, the existence of mineral salt.

Nowadays, new types of recyclable catalysts have drawn researchers' attention. The effects of many factors on the yield of ECH is also studied.

Zhang et al. [153] have investigated the catalytic performance of alkaline earth metal nitrate/ γ -Al₂O₃ and alkaline earth metal chloride/ γ -Al₂O₃ for the cyclization of DCH to ECH. By investigating the effect of nitrate as a precursor on the reaction, 10BaO/ γ -Al₂O₃ has a better catalytic performance. The analysis showed that 10BaO/ γ -Al₂O₃ had poor catalytic performance due to its lower specific surface area and excessive weak alkaline sites. By investigating the effect of chloride as a precursor on the reaction, 10MgCl₂/ γ -Al₂O₃ has better catalytic performance due to its increased alkali content compared to the other catalysts. The optimal catalyst was proved to be the 10BaO/ γ -Al₂O₃ due to its better catalytic stability by further comparative analysis.

Zou et al. [154] investigated the semi-continuous biotransformation of 1,3-DCP to ECH using epoxy resin ES-103B-immobilized halohydrin dehalogenase as biocatalyst in a recirculating packed bed reactor (RPBR), an ECH yield of 94.2%, was obtained with average productivity of 5.2 g/L/h.

5. Conclusions

Known as one of the crucial function groups in chemistry, the oxirane group is commonly synthesized through the oxidation of unsaturated groups. In order to review the research progress for the synthesis of oxirane, three different epoxidized family molecules were mainly studied and produced with homogeneous, heterogeneous or enzymatic catalysts in the gas, liquid and liquid–liquid reaction systems, and summarized.

In this review, the main catalytic methods for the synthesis of ethylene/propylene oxides, epoxidized vegetable oils and epichlorohydrin, and the advantages and disadvantages of the catalytic systems, were evaluated. Moreover, aiming for eco-friendly and efficient oxirane synthesis, simplified and directed catalytic processes have attracted researchers' attention. Novel catalysts and updated techniques were explored to prepare oxirane groups, such as AIER catalyst, Ti-based catalyst and composite catalyst with several metallic elements.

For the classical and industrial ways, the complex reaction systems provide more harmful byproducts (e.g., chlorine salts) and need more energy. Thus, improving manufacturing production with more efficient approaches will still be the main objective in future years. Novel ways (e.g., one-step synthesis of epichlorohydrin and epoxidation with AIER) face other challenges, such as comparably lower conversion, catalytic efficiency and selectivity issues. Environmental issues still need preferable solutions for less harmful coproducts and milder reaction conditions. Besides exploring suitable synthetic techniques, seeking green catalytic routes and potential renewable raw materials for the epoxidation reaction is also very meaningful to broaden our knowledge in this growing field.

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visualization, Y.M., F.T., A.F.A., X.C., V.R., P.T. and S.L.; project administration, V.R., P.T. and S.L. All authors have read and agreed to the published version of the manuscript.

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