

# A Comprehensive Review on Advancing Greener Epoxidation: Mechanistic Insights and Sustainable Frontiers

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## ABSTRACT

**Introduction:** In organic synthesis, epoxidation is essential for creating chemical, polymer, and pharmaceutical intermediates. Conventional techniques, such as peracid-based and metal-catalyzed epoxidations, are effective but have toxicity and environmental issues.

**Method:** By examining recent advancements in green solvents, biomimetic catalysis, AI-driven catalyst design, metal-catalyzed, peroxide-based, enzymatic, photocatalytic, electrochemical, and organocatalytic processes, this paper compares traditional approaches with more environmentally friendly alternatives.

**Result:** While hydrogen peroxide and peracids enhance atom economy, catalysts made of titanium, manganese, and vanadium are still essential. High selectivity and low energy consumption are demonstrated by electrochemical, photocatalytic, and enzymatic techniques. Green solvents and bio-based feedstocks improve eco-efficiency even more.

**Discussion:** Conventional epoxidation techniques such as peracid and metal-catalyzed reactions are being eclipsed by greener and energy-efficient methods. Use of renewable energy, biotechnology and machine-learning in catalyst design is anticipated to transform the discipline to make epoxidation more scalable, environmentally friendly, and staple in green chemistry.

**Keywords:** Sustainable Epoxidation, Mechanistic Pathways, Catalysis, Green Chemistry, Emerging Trends

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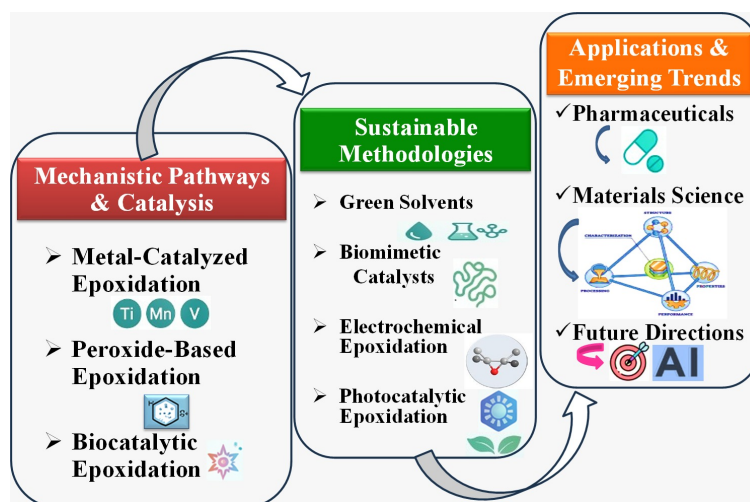
## Highlights

- Metal-catalyzed epoxidation is made efficient by titanium and vanadium catalysts.
- H<sub>2</sub>O<sub>2</sub> promotes environmentally benign peroxide epoxidation.
- Minimal waste and high selectivity are guaranteed by enzymatic epoxidation.
- Greener alternatives to epoxidation are encouraged by deep eutectic solvents.
- AI speeds up the process of finding sustainable catalysts for epoxidation.

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## Graphical Abstract



## 1. INTRODUCTION

Epoxidation is a general and very important reaction in organic chemistry, used extensively in synthesizing valuable intermediates for industrial and research purposes. It is a process where an alkene has been converted into an epoxide, a three-membered cyclic ether, by incorporating an oxygen atom. Epoxides are fundamental building blocks in synthesizing fine chemicals, drugs, and polymers. This review discusses the mechanistic routes of epoxidation, the variety of reagents used, and the widening vistas of greener and sustainable methods. Additionally, epoxidation is a chemical reaction converting a double bond to an epoxide. The synthetic and biological relevance of epoxides stems from their strained ring structure, which imparts significant reactivity. Naturally occurring and synthetic epoxides are integral to the structures of pharmaceuticals, agrochemicals, and specialty polymers. Epoxides also play necessary roles in industries, like adhesives, paints, and matrix materials (Phinyocheep, 2014; Chemistry LibreTexts, n.d.). Among traditional approaches, peracid-mediated epoxidation remains prevalent, with oxidants such as meta-chloroperoxybenzoic acid (m-CPBA), peracetic acid, and performic acid facilitating oxygen transfer via a concerted cyclic transition state. This method yields the desired epoxide alongside a carboxylic acid byproduct. The intermediate then decomposes, producing the epoxide and a carboxylic acid byproduct (Royals, 1954; Streitwieser & Heathcock, 1981; Vollhardt & Schore, 2007; Carey & Sundberg, 2007).

The most common method relies on oxone, a potent oxidizing reagent, a peroxydisulfate potassium triple salt. This reaction forms an oxirane intermediate that is hydrolyzed to form an epoxide. Oxone has advantages over peracids regarding cost, accessibility, and ecological compatibility (Vollhardt & Schore, 2007; Dehestani et al., 2005; Bales et al., 2005). Metal-catalyzed epoxidation is a standard method, involving metal complexes like titanium, molybdenum, and tungsten as catalysts to energize peroxide reagents. This process has advantages over

conventional peracid and oxone-reagent-based processes, including more benign reaction conditions and higher selectivity towards targeted alkenes (Lane & Burgess, 2003; Chua et al., 2012). Asymmetric epoxidation converts non-chiral alkenes into chiral epoxides, which is helpful in synthesizing enantiopure compounds, an important factor in pharmaceutical and agrochemical manufacture. Reactionism is mainly accomplished with chiral catalysts, such as chiral metal complexes and organocatalysts (Katsuki & Sharpless, 1980; Sharpless et al., 1983; Bryce, 1986; Bergin, 2015).

Aside from alkene epoxidation, other epoxidation reactions include converting carbonyl compounds to epoxides through an oxirane intermediate. Such an approach is often employed in synthesizing epoxide-bearing natural products (Triandafillidi et al., 2021). Essentially, epoxidation is an organic chemistry foundational reaction with extensive usage in natural and artificial compound synthesis. Primary techniques involve peracid, oxone, and metal-catalyzed epoxidation, with asymmetric epoxidation being pivotal in enantio-pure compound synthesis. Continued research drives advances in epoxidation methods and catalysts, advancing the discipline (Vollhardt & Schore, 2007). Current review insight shaping the fundamental processes driving epoxidation reactions, highlighting leading catalytic systems and the rules of reaction selectivity.

## 2. MECHANISTIC INSIGHTS INTO EPOXIDATION REACTIONS

Epoxidation reactions tend to go through electrophilic oxygen transfer to an alkene. The usual mechanisms include a peracid-mediated oxidation, a metal-catalyzed epoxidation, and enzyme-catalyzed reactions.

## 2.1. Peracid Epoxidation

One of the traditional methods is the application of peracids like m-chloroperoxybenzoic acid (m-CPBA). The mechanism is concerned with the peracid donating an oxygen atom to the alkene, leading to high regioselective epoxide formation (Streitwieser & Heathcock, 1981;

Vollhardt & Schore, 2007).

## 2.2. Metal-Catalyzed Epoxidation

Transition metal catalysts—such as those based on titanium, manganese, and ruthenium—are pivotal in promoting epoxidation using oxidants like hydrogen peroxide or molecular oxygen. A landmark in this domain is the Sharpless asymmetric epoxidation, which employs titanium isopropoxide in combination with tartrate esters to achieve highly enantioselective transformations, critical for chiral pharmaceutical synthesis (Srouf et al., 2013; Adolffson, 2005).

## 2.3. Oxone-Mediated Epoxidation

Oxone, a triple salt of potassium peroxydisulfate, is a versatile oxidizing agent commonly employed in epoxidation reactions. Upon reaction with Oxone, alkenes first give an oxirane intermediate, which then gets hydrolyzed to produce the corresponding epoxide. This reaction is an important part of several synthetic routes involving the formation of epoxides. Oxone is more readily available, cheaper, and has a better environmental footprint than peroxyacids. The reaction's selectivity depends upon the alkene's substitution pattern and the reaction conditions used (de la Mare & Bolton, 2008).

## 2.4. Asymmetric Epoxidation

Asymmetric Epoxidation is a beneficial method for synthesizing chiral epoxides, which are key intermediates in synthesizing drugs and natural products. The process is also important for generating chiral building blocks employed in drug discovery and development. Their action depends on a chiral catalyst that facilitates the selective formation of one enantiomer of the epoxide. A few typical examples of asymmetric Epoxidation are the synthesis of chiral epoxides like limonene oxide, chalcone oxide, and styrene oxide (Jacobsen et al., 1991).

## 2.5. Base-Catalyzed Epoxidation

Base-catalyzed Epoxidation is a standard method for the synthesis of epoxides from alkenes. It is an important method of preparation of epoxides, which are used as intermediates in manufacturing surfactants, detergents, and plasticizers. In the reaction, a base catalyst activates an oxidizing agent, which reacts with the alkene to give the desired epoxide. Examples of base-catalyzed Epoxidation are the formation of compounds like butadiene oxide, glycidol, and phenylglycidyl ether (Shi, 2004).

## 2.6. Enzymatic Epoxidation

Enzymes like cytochrome P450 monooxygenases and peroxidases provide a biocatalytic pathway to epoxide formation under mild and environmentally friendly conditions. These enzymatic reactions have excellent regio- and stereoselectivity and are well suited for pharmaceutical and biotechnological applications (Shi, Y. 2001).

## 2.7. Reagents and Catalysts in Epoxidation

Epoxidation reactions employ various reagents and catalysts to make them more efficient and selective. Typical reagents are peracids (e.g., meta-chloroperoxybenzoic acid (m-CPBA), performic acid), hydrogen peroxide-based systems (e.g., H<sub>2</sub>O<sub>2</sub> in the presence of tungstate or titanium catalysts), halohydrin intermediates (treated with base to achieve *in situ* Epoxidation), and molecular oxygen (used in aerobic oxidation catalyzed by metal complexes). The reagent of choice depends on the heterocyclic substrate and the regioselectivity desired for the epoxidation reaction (Lane & Burgess, 2003). The data reported in **Table 1** summarizes advantages, applications and green perspective of some of the typical reagents and catalysts used in epoxidation reactions.

**Table 1:** Summary of important reagents and catalysts used in epoxidation reactions.

Sr. No.	Reagent/Catalyst Type	Advantages	Applications	Green Chemistry Perspective	References
1	Peracids (m-CPBA, peracetic acid (PAA), perbenzoic acid (PBA))	High reactivity, easy to handle	General alkene epoxidation	Moderate atom economy; generates stoichiometric waste	Shi, 2004
2	Metal complexes (molybdenum, tungsten catalysts)	High selectivity, mild conditions	Asymmetric & heterocyclic epoxidation	Catalytic; but metals may pose toxicity concerns	Kholdeeva, 2009
3	Organic peroxides (tert-butyl hydroperoxide (TBHP), hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> ))	Economical, safe	Broad synthetic applications	H <sub>2</sub> O <sub>2</sub> is green; TBHP requires handling precautions	Climent, M. J., 2014
4	Miscellaneous (Oxone, dimethyldioxirane (DMDO))	High selectivity, clean profiles	Electron-rich alkenes	Oxone: user-friendly; DMDO: unstable but clean byproducts	Shi, 2001

These reagents contribute significantly to epoxidation chemistry through presenting varying amounts of reactivity, selectivity, and ease of use, thus making it possible to provide specific methods for diverse synthetic

purposes (Shi, 2001).

## 3. APPLICATIONS OF EPOXIDATION REACTIONS

Epoxidation reactions are central to wide-ranging areas of

chemistry because of the reactivity and versatility of epoxides, which stem from the strain within their three-membered cyclic ether system. Their range of applications ranges from synthetic intermediates to functional materials and bioactive molecules.

### 3.1. Organic Synthesis

Epoxides are highly reactive organic synthesis intermediates, which go through regio- and stereoselective processes to give a range of functionalized compounds. The compounds are mainly: alcohols, glycolols, and amines.

**3.1.1. Alcohols:** Acid- or base-catalyzed hydrolysis of epoxides gives alcohols with Markovnikov or anti-Markovnikov selectivity, respectively.

**3.1.2. Glycols:** Reaction with water under acidic conditions gives 1,2-diols (glycols), important in polyol and biomolecule synthesis.

**3.1.3. Amines:** Epoxides react with ammonia or amines through nucleophilic ring opening to give  $\beta$ -amino alcohols, key intermediates in pharmaceuticals and agrochemicals.

**3.2. Polymer Chemistry:** Epoxidized monomers play a significant role in forming high-performance polymers and coatings. Which includes:

**3.2.1. Mechanical Strength and Stability:** High crosslink density improves toughness and adhesion, which is critical for aerospace and automotive applications.

**3.2.2. Chemical and Corrosion Resistance:** Crosslinked epoxides resist solvents and environmental degradation and are well-suited for protective coatings.

**3.2.3. Thermal Stability:** High glass transition temperatures facilitate application in electronics and composites.

**3.2.4. Sustainability:** Bio-based epoxidized oils and lignin derivatives offer environmentally friendly, low-VOC options.

**3.2.5. Functional Tailoring:** Structural modification laws for application-specific marine, medical, and electronic application properties.

### 3.3. Medicinal Chemistry

Epoxide-bearing compounds are central to drug synthesis because they can bring stereochemical intricacy and functional diversity (Wang&Tang,2013).

**3.3.1.  $\beta$ -Amino Alcohols:** Generated via epoxide-amine reaction; central to  $\beta$ - blockers such as propranolol (Ojima, 2019).

**3.3.2. Glycols:** Diol intermediates are precursors to anticancer drugs such as paclitaxel, prepared by selective epoxidation (Nicolaou et al., 1994).

**3.3.3. Chiral Alkylation:** Epoxides allow enantioselective alkyl at ion during the synthesis of

optically pure drugs (Zhang et al., 2016).

**3.3.4. Antimicrobial Agents:** Epoxide scaffolds, such as epoxomicin and azole antifungals, possess strong biological activity (Groll et al., 2006).

**3.3.5. Steroid Derivatives:** Epoxidation enables steroid functional diversification for contraceptives and anti-inflammatory agents. These reactions allow access to diverse bioactive molecules, making epoxides extremely useful in drug discovery (Ding et al., 2011).

### 3.4. Agricultural Chemistry

In agrochemical development, epoxides are involved in the synthesis of highly bioactive fungicides and pesticides. Their reactive functionality facilitates the development of new crop protection agents to improve yield and manage resistance (Casida, 2009).

## 4. GREENER AND MORE SUSTAINABLE EPOXIDATION STRATEGIES

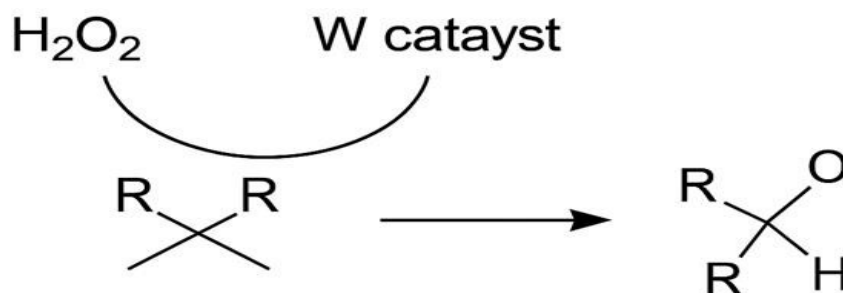
The evolution of greener epoxidation methods makes sustainable epoxidation output. Aqueous hydrogen peroxide-based systems represent an environment-friendly approach to oxidation processes compared to traditional oxidation methods, which abandon toxic peracids and produce only water as a waste byproduct. These systems use aqueous hydrogen peroxide ( $H_2O_2$ ) as an oxidizing agent with the support of solid catalysts, minimizing waste and increasing efficiency (Kamata et al., 2010).

### 4.1. Tungstate-Catalyzed Hydrogen Peroxide Epoxidation

Tungstate-catalyzed hydrogen peroxide ( $H_2O_2$ ) epoxidation is a prospective and sustainable protocol for the selective oxidation of alkenes. The method takes advantage of the high reactivity and environmentally friendly character of  $H_2O_2$ , which disintegrates into water as the exclusive byproduct. Sodium tungstate ( $Na_2WO_4$ ) or tungstic acid ( $H_2WO_4$ ) are usually used as precatalysts that form in situ active peroxotungstate species under mild conditions. These catalysts are further tunable with ligands or can be supported on solid materials to increase selectivity and recyclability. The mechanism generally generates mono- or diperoxo species that are electrophilic oxidants, which transfer an oxygen atom to the alkene and then regenerate the catalyst. Solvent systems like water, acetonitrile, or alcohol are used, with aqueous media especially beneficial from the green chemistry perspective. Additives such as chelating ligands or phase-transfer agents can be added to influence solubility and reactivity. However, careful attention must be taken to control the possible risks involved in  $H_2O_2$  concentration and the presence of transition metals and facilitate process scalability and longevity of the catalyst. In general, this system is highly consistent with green chemistry principles—exhibiting excellent atom economy, low energy intensity, minimal waste generation, and recoverability of the catalytic system—but needs careful optimization for industrial application (Kholdeeva et al., 2006; Nooraeipour et al., 2011; Sheldon & Arends, 2004).

**Figure 1** explains Tungsten-based catalytic systems with aqueous hydrogen peroxide as an oxidant. This combination is frequently employed in various oxidation reactions. The tungsten catalyst facilitates the reaction, while the hydrogen peroxide provides the oxidizing

power. These systems' specific applications and efficiency depend on factors like the tungsten source, the reaction conditions (temperature, pH, etc.), and the substrate being oxidized.

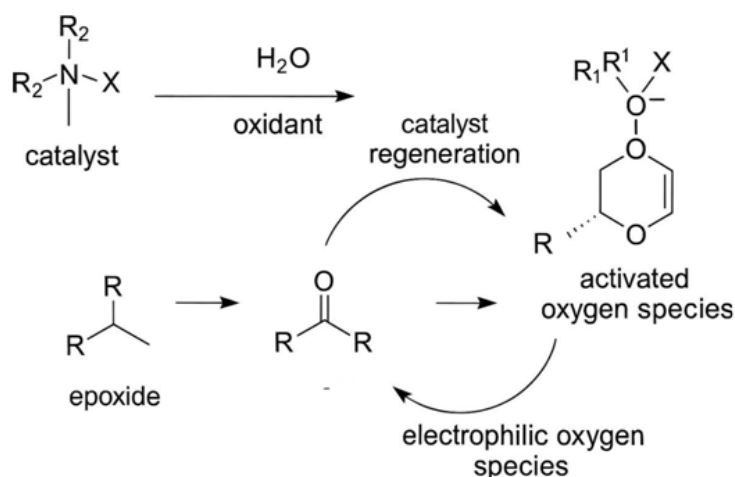


**Figure 1:** Schematic illustration for tungsten-based catalytic systems, with aqueous hydrogen peroxide functioning as the oxidant.

#### 4.2. Metal-Free Catalytic Systems

Metal-free catalytic systems, primarily biological process-inspired ones, have received growing interest as more sustainable alternatives to conventional metal-based catalysts that carry environmental and financial problems. Organocatalytic epoxidation is one of the key methods in this class that provides a greener and more environmentally friendly epoxide route by using non-metallic catalysts combined with environmentally friendly oxidants like hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). One such

prominent example is Dakin–West-type epoxidation catalysis using highly enantioselective iminium salts, which proceed under benign conditions and produce only water as a byproduct, which fits very much into the green chemistry agenda. They are prepared and tested in the catalytic asymmetric epoxidation of unfunctionalized alkenes, giving up to 95% yield. **Figure 2** presents the catalytic cycle of an iminium salt-based epoxidation pathway.



**Figure 2:** Schematic illustration for iminium salt-catalyzed epoxidation via a Dakin–West-type pathway.

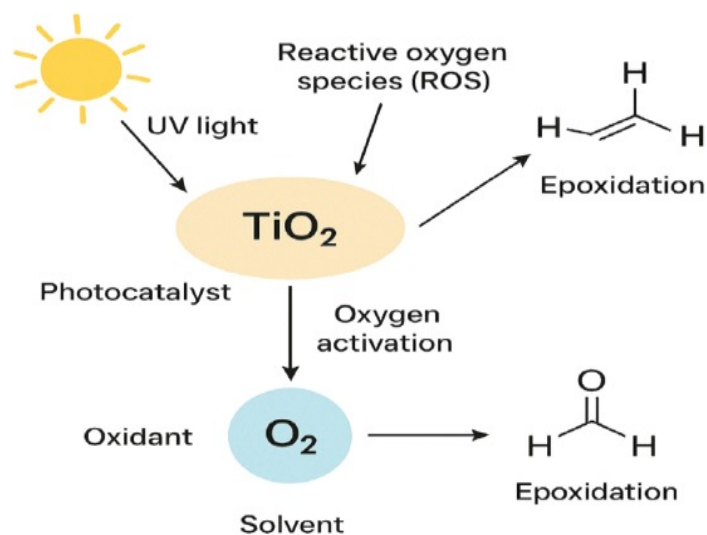
The catalysts are typically derived from organic iminium salts or urea-derived compounds and activate H<sub>2</sub>O<sub>2</sub> to generate reactive electrophilic oxygen species that transfer an oxygen atom to the alkene substrate highly region and stereoselectively. The organocatalyst is recovered at the termination of the cycle for a closed and effective catalytic cycle (Teles et al., 1998; Tong et al., 2005). Despite their many benefits, such as metal-free conditions, high tolerance of functional groups, and applicability to the pharmaceutical industry, care should be exercised regarding organocatalyst stability and scalability for industrial processes, substrate scope limitations and reaction rates under aqueous conditions.

#### 4.3. Photocatalytic epoxidation using TiO<sub>2</sub> and molecular oxygen

Photocatalytic epoxidation is an innovative, green method of alkene oxidation by utilizing light energy—ideally sunlight—to activate mild oxidants like molecular oxygen (O<sub>2</sub>), thus reducing dependence on toxic reagents. Among the numerous photocatalysts reported, titanium dioxide (TiO<sub>2</sub>) is still the most widely researched because of its low price, excellent stability, and strong photocatalytic activity under ultraviolet (UV) illumination. Under photo-excitation, TiO<sub>2</sub> produces reactive oxygen species (ROS), i.e., superoxide anions and hydroxyl radicals, that selectively epoxidize alkenes under mild, green

conditions. Other visible-lightactive catalysts, such as doped  $\text{TiO}_2$  or graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ), have broadened the scope of these systems to be used with solar

irradiation more effectively. **Figure 3** provides a schematic of the  $\text{TiO}_2/\text{O}_2$ -based photocatalytic mechanism.

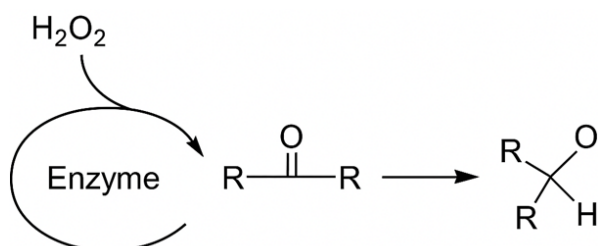


**Figure 3:** Schematic illustration for Photocatalytic Epoxidation using Titanium Dioxide ( $\text{TiO}_2$ ) and Molecular Oxygen ( $\text{O}_2$ ).

Usually performed in environmentally friendly solvents such as water or ethanol, the reactions align with green chemistry principles by using nontoxic oxidants, environmental operational conditions, and incorporation of renewable energy (Shi et al., 2013). Nevertheless, even though they hold much promise, these systems must be well optimized to counter restrictions such as  $\text{TiO}_2$ 's UV-light dependent nature, comparatively low rates of reaction, and possible issues with product separation and catalyst recovery at large scale. Ongoing research into catalyst design and visible-light activation continues to be key to advancing the industrial relevance of photocatalytic epoxidation processes.

#### 4.4. Enzymatic Epoxidation Via Peroxygenase-Catalyzed Systems

Enzymatic epoxidation offers a biocatalytic alternative to traditional oxidation methods, employing enzymes such as unspecific peroxygenases (UPOs) and cytochrome P450 monooxygenases to catalyze the selective epoxidation of alkenes using hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as an oxidant. This approach is highly compatible with green chemistry principles, as it operates under mild aqueous conditions, produces only water as a byproduct, and eliminates the need for metal catalysts and organic solvents. **Figure 4** shows that Peroxygenases are enzymes that catalyze the epoxidation of alkenes using hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).



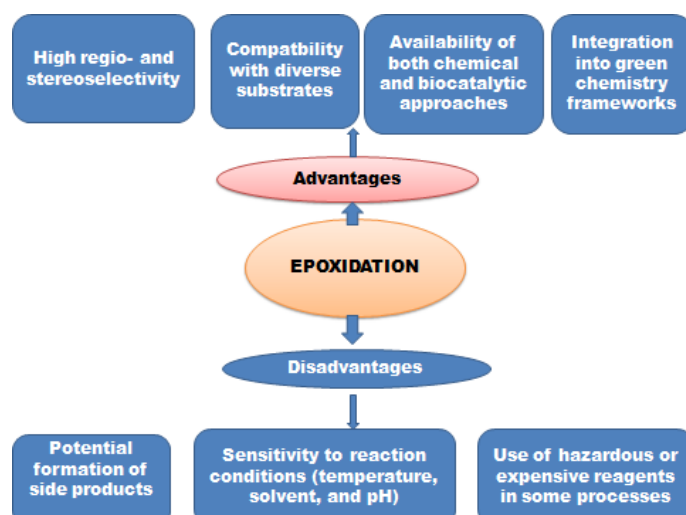
**Figure 4.:** Schematic illustration for peroxygenase-catalyzed epoxidation with hydrogen peroxide.

The mechanism involves the enzymatic activation of  $\text{H}_2\text{O}_2$  to generate a reactive oxo-iron species capable of transferring an oxygen atom to the alkene in a regio- and stereoselective manner. These systems demonstrate high efficiency and substrate specificity, particularly for styrenes and terpenes, making them attractive for applications in pharmaceutical and fine chemical synthesis (Teles et al., 1998). However, while enzymatic systems are inherently eco-friendly and biodegradable, challenges include enzyme stability, narrow operational pH ranges,

potential substrate limitations, and the cost of enzyme production. Thus, epoxidation, the process of adding an epoxide group (a three-membered ring containing one oxygen atom and two carbon atoms) to an alkene, is crucial in synthesizing various chemicals, including pharmaceuticals and fine chemicals and a promising area of research, aiming to develop more efficient and selective catalysts for various industrial applications. Continuous development in enzyme engineering and process optimization is essential to fully realize the potential of

enzymatic epoxidation as a scalable, green oxidation platform. Advantages include creating various stereoisomers, with high regio- and stereoselectivity achievable through carefully selecting reagents and catalysts, such as peroxy acids or metal-catalyzed systems. This precision allows for the controlled formation of chiral epoxides, which are crucial for pharmaceuticals and fine chemicals. However, disadvantages include potential unwanted side reactions, hazardous reagents like peracids, and the cost associated with some catalysts and specialized equipment. Furthermore, the choice of epoxidation method

depends heavily on the substrate's nature, as different functional groups can affect reactivity and selectivity, **Figure 5** provides a comparative overview of different epoxidation strategies. Metal-based, organocatalytic, photocatalytic, and enzymatic systems are contrasted regarding sustainability, selectivity, operational complexity, and scalability. This visualization highlights the versatility of epoxidation chemistry while emphasizing the need for strategic choice of method depending on substrate type and desired application.



**Figure 5:** Schematic illustration for advantages and disadvantages of various epoxidation reactions.

## 5. APPLICATIONS AND EMERGING TRENDS

The advancement of greener epoxidation technologies has had far-reaching implications, such as organic synthesis, polymer synthesis, and pharmaceutical production. Although classical approaches hold value, recent innovation has increasingly promoted methods consistent with green chemistry concepts. Notably, the use of environmentally friendly oxidants—e.g., hydrogen peroxide and molecular oxygen—has made possible more sustainable synthesis of complex molecules, such as steroids, insect pheromones, glycosidase inhibitors, and critical pharmaceutical intermediates like taxol and artemisinin. At the same time, breakthroughs in catalytic systems—stretching from chiral organocatalysts and bio-based enzymes to nanostructured metals and photocatalytic materials—have dramatically enhanced both selectivity and efficiency under milder conditions. The move toward bio-based feedstocks, e.g., vegetable oils and fatty acids, also increasingly focuses on circular economy approaches, particularly for synthesizing epoxide-functionalized polymers and prospective biofuel intermediates. However, translating these methodologies into practical industrial scales requires sensitive optimization, especially for catalyst recyclability, scalability of reactions, and substrate generality. Notwithstanding persistent issues, the overall improvement in catalyst design, more sustainable oxidants, and renewable feedstocks places epoxidation as a cornerstone reaction in future-oriented green chemistry (Phinyocheep, 2014; Triandafillidi et al., 2021; Srou et

al., 2013; Chua et al., 2012). Nevertheless, large-scale translation necessitates further optimization in catalyst recyclability, reaction efficiency, and substrate diversity.

## 6. CONCLUSION

The ongoing advancement of greener epoxidation technologies holds significant implications for organic synthesis, polymer production, and pharmaceuticals. Future research will increasingly focus on integrating green catalysis, bio-based feedstocks, and renewable energy sources to develop processes that are not only cost-effective and scalable but also truly sustainable. Significant breakthroughs in catalytic systems, ranging from chiral organocatalysts to nanostructured metals and photocatalytic materials, have substantially enhanced reaction selectivity and efficiency under milder conditions. Concurrently, the shift towards bio-based feedstocks, such as vegetable oils, strongly supports circular economy approaches, particularly for developing epoxide-functionalized polymers and biofuels. The integration of biotechnology, photocatalysis, and flow chemistry, coupled with the application of machine learning and AI in catalyst design, is poised to redefine epoxidation processes. This will lead to drastically reduced environmental impact and significantly improved efficiency, solidifying epoxidation's role as a cornerstone reaction in future-oriented green chemistry.

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