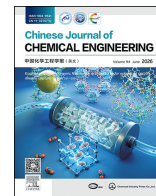




Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Review

Advancing the industrial production of propylene oxide toward inherent safety and environmental sustainability: A mini review

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ARTICLE INFO

Article history:

Received 3 June 2025

Received in revised form

16 October 2025

Accepted 17 October 2025

Available online 28 January 2026

Keywords:

Propylene oxide

Inherent safety

Gas-phase epoxidation

Microreactor

Electro-oxidation

ABSTRACT

Propylene oxide (PO) is an important chemical intermediate that has experienced a continuous rise in annual demand. Traditional processes such as the chlorohydrin process and hydrogen peroxide-propylene oxide process (HPPO) are gradually being phased out due to environmental pollution, complex procedures, and economic inefficiencies. The discovery of the titanium silicalite-1 zeolite has markedly improved the activity and selectivity of the HPPO process, facilitating its industrial application. Nonetheless, the costs associated with the storage and transportation of H₂O₂, along with its safety risks during the process, continue to pose a limitation. This paper presents a comprehensive review of the current industrial status, risk analysis, and advancements in inherent safety research concerning the production of PO. The review systematically assesses the advantages and limitations of various production processes, focusing on safety, environmental impact, and lifecycle risk analysis. The gas-phase epoxidation of propylene and electrochemical epoxidation technology have become prominent research areas due to their mild reaction conditions, streamlined processes, and risk reduction at the source. These approaches provide new directions for inherently-safer PO production. Future efforts should prioritize addressing challenges in catalyst performance and process integration to propel the PO industry toward greater efficiency, safety, and sustainability.

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1. Introduction

1,2-Propylene oxide, commonly known as propylene oxide (PO), is an essential chemical intermediate derived from propylene and accounts for approximately 7% of global propylene consumption, ranking as the second most significant propylene derivative. PO primarily contributes to the production of organic raw materials, including polyether polyols (PPG), propylene carbonate (PC), and dimethyl carbonate (DMC), which have wide-ranging applications across various industries such as food processing, tobacco treatment, cosmetic formulations, energy storage and pharmaceutical manufacturing [1].

The consumption and production capacity of PO has grown gradually in recent years, as shown in Fig. 1(a). China's PO consumption reached 3.39 million metric tons in 2022, with primary end-use sectors comprising furniture (36%), home appliances (16%) and automotive components (8%) [2]. As PO's largest downstream consumer product, PPG represents 73% of total PO consumption and serves as the core driver of PO demand. Currently, the most critical downstream product of PPG is polyurethane (PU). As an emerging organic polymer material, PU combines exceptional performance with environmental benefits and energy-saving characteristics. Widely used in the light manufacturing, electronics, textile coatings, and aerospace engineering industries, its utilization continues to expand in response to evolving market demands in recent years. Additionally, DMC constitutes 15% of PO derivatives and has emerged as a pivotal growth sector. DMC is a low-toxicity and eco-friendly organic synthesis intermediate with versatile applications, which can be

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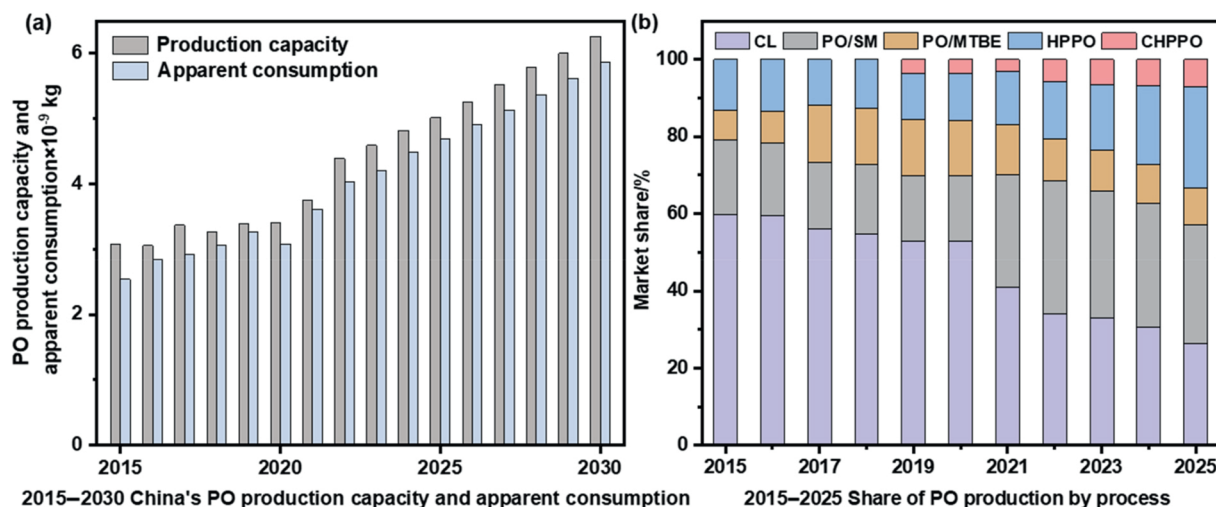


Fig. 1. (a) Capacity and apparent consumption of PO from 2015 to 2025 and forecast from 2026 to 2030; (b) proportion of PO produced by different processes from 2015 to 2025.

used to produce derivatives such as polycarbonate and anisole. It can also serve as a critical electrolyte solvent in lithium-ion batteries, making it a critical raw material for core components of new energy vehicles.

The global PO market size was valued at USD 22.0 billion in 2024. Looking forward, IMARC Group estimates the market to reach USD 33.1 billion by 2033, exhibiting a CAGR of 4.6% during 2025–2033. In 2022, China's PO industry reached a production capacity of 4.5 million metric tons with an output of 3.7 million metric tons, yielding an average plant utilization rate of 82% [3]. As shown in Fig. 1(b), the chlorohydrin (CL) process, the earliest industrialized production method, has long maintained a market share exceeding 50%. However, due to its environmentally unfriendly nature and tightening regulations [4], this method has gradually phased out. In contrast, the co-oxidation process provides environmental benefits and comprises two main pathways: PO/styrene monomer (SM) and PO/methyl *tert*-butyl ether (MTBE). However, this process requires substantial capital expenditure, sophisticated equipment, and complex byproduct conversion processes, making it economically viable primarily for large petrochemical corporations. Among contemporary methods, the direct oxidation process—encompassing HPPO (hydrogen peroxide to propylene oxide) and CHPPO (cumene hydro-peroxide to propylene oxide)—better aligns with green chemistry principles. Its simplified workflow and superior atomic efficiency have accelerated industrial implementation. Meanwhile, emerging research focuses on intrinsically safer processes such as gas-phase hydrogen–oxygen direct oxidation, microreactor technology, and electrochemical oxidation approaches.

2. Status of PO Industrial Production

Globally industrialized PO production methods currently comprise three principal approaches: the CL process, co-oxidation process (including PO/SM and PO/MTBE), and direct oxidation process (encompassing HPPO and CHPPO), as shown in Fig. 2. The CL process demonstrates advantages in selectivity and capital efficiency but suffers from intrinsic limitations, including equipment corrosion and hazardous byproduct generation due to its reliance on toxic chlorine reagents. These environmental drawbacks, exacerbated by tightening regulations, are accelerating its industrial phase-out. The co-oxidation process resolves corrosion and

pollution concerns but introduces operational complexities through multi-step workflows, substantial infrastructure investments, and strict feedstock quality specifications. Although byproducts (e.g., styrene or MTBE) can offset some costs, the economics of PO production remain contingent on fluctuating demand for co-products. Modern industry prioritizes the development of sustainable processes characterized by minimal pollution, high atomic efficiency, simplified workflows, and byproduct-free outputs. The direct oxidation process, exemplified by hydrogen peroxide (H_2O_2)-based methods, has emerged as a promising candidate. Early implementation barriers related to catalyst performance had not been overcome until the discovery of titanium silicate-1 (TS-1) zeolite, which significantly enhanced the activity and selectivity of HPPO under mild and environmentally friendly conditions [5,6]. This breakthrough has enabled industrial-scale implementation [7]. However, the persistent challenge involves the transportation-related safety risks and increased costs associated with H_2O_2 . To mitigate this, on-site H_2O_2 production facilities are often required, which introduces additional steps and cost overheads.

2.1. Chlorohydrin process

The CL process was first developed in the 1920s. In 1931, Union Carbide Corporation (USA) constructed the world's first industrial-scale PO production facility using this method [8]. The primary raw materials for this process are propylene, H_2O , and Cl_2 . The production involves two key steps, as shown in Fig. 3 [9]. In the chlorohydrination step, propylene reacts with hypochlorous acid (HClO) in a CL reactor to synthesize chloropropanol intermediates. Subsequent saponification treatment with sodium hydroxide (NaOH) or calcium hydroxide ($\text{Ca}(\text{OH})_2$) converts these intermediates into crude PO, which undergoes distillation and purification to eliminate residual H_2O , HCl , and other contaminants generated during saponification. Additionally, precise pH control during purification is essential to suppress hydrolysis byproducts and maintain final product selectivity. Despite its advantages—mature technology, simple equipment, and low purity requirements for propylene—the CL process consumes large amounts of chlorine (1.5 tons per ton of PO), water, and lime, while generating significant wastes including ≥ 40 t of chlorine-containing wastewater and >2 t of CaCl_2 residue per ton of PO produced [10]. These byproducts cause severe environmental

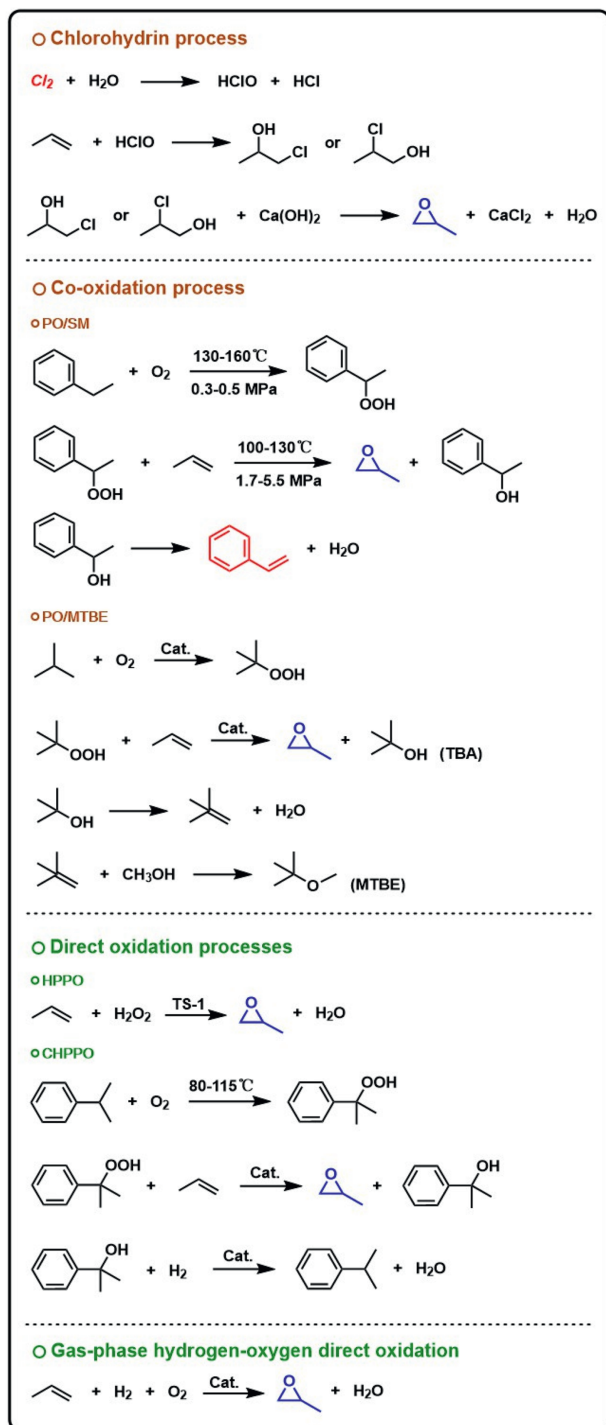


Fig. 2. Various production processes of PO.

pollution and equipment corrosion. Consequently, these detrimental factors prompted China's 2011 regulatory prohibition on new CL-based PO production facilities [4].

2.2. Co-oxidation process

Co-oxidation processes primarily include the PO/SM process and the PO/MTBE process. The PO/SM process, also known as the ethylbenzene hydroperoxide (EBHP) method, utilizes ethylbenzene and propylene as primary feedstocks. The PO/SM process

involves two key steps, as shown in Fig. 4 [11]. For peroxidation, ethylbenzene undergoes oxidation with oxygen to form EBHP. In the epoxidation step, EBHP reacts with propylene in the presence of catalyst [12], producing crude PO and the byproduct 2-phenylethanol. The byproduct is further dehydrated to yield SM. The PO/SM co-oxidation process was first successfully developed by Halcon Corporation (USA) and achieved industrialization in 1969 [13].

The PO/MTBE process operates on a similar principle to PO/SM method, with isobutane and propylene as its primary feedstocks. As illustrated in Fig. 5 [14], in the peroxidation step, isobutane reacts with oxygen to form *tert*-butyl hydroperoxide (TBHP). For the epoxidation step, TBHP undergoes a reaction with propylene to produce PO. The byproduct, *tert*-butyl alcohol (TBA), is further reacted with methanol to generate methyl MTBE. Some plants bypass MTBE synthesis and instead purify TBA directly as a co-product, producing PO and TBA as paired outputs. Compared to the CL process, this method eliminates chlorine usage, reduces environmental pollution, and minimizes equipment corrosion. However, it requires substantial raw material consumption and generates large volumes of co-products. For example, when the PO/SM process produces 1 t of PO, it consumes ~3.2 t of ethylbenzene and yields ~2.25 t of styrene, while the PO/MTBE process consumes ~2.8 t of isobutane and yields ~2.5 t of TBA [15]. The economic sustainability remains inherently vulnerable to co-product market flexibility due to these operational interdependencies.

2.3. Direct oxidation processes

The HPPO process and CHPPO process are the two direct oxidation methods currently applied in industry. The HPPO process employs H_2O_2 to directly oxidize propylene, producing PO and water through a simplified workflow. The discovery of TS-1 molecular sieves marked a breakthrough, significantly enhancing the reaction's selectivity and activity [5,6], which enabled the industrial adoption of HPPO technology. For instance, Dow Chemical established a $390000\text{-t}\cdot\text{a}^{-1}$ HPPO plant in Thailand, which commenced operations in 2012. In 2022, researchers from the Dalian Institute of Chemical Physics, Chinese Academy of Sciences and Tianjin Dagu Chemical Co., Ltd. jointly developed an innovative liquid–solid circulating fluidized bed hydrogen peroxide direct oxidation process (FHPPPO). In a 100-t pilot facility, this process achieved a H_2O_2 conversion rate of 99.7%, PO selectivity of 98.2%, H_2O_2 utilization efficiency of 99.9%, and product purity of 99.95%, with its space-time yield surpassing global counterparts by 2–3 times [16]. Additionally, the homogeneous catalyst methyltrioxorhenium (MTO) has been demonstrated to catalyze the epoxidation of olefins using H_2O_2 under relatively mild conditions [17]. Researchers at the University of Kansas further discovered that pyridine-N-oxide (PyNO) could stabilize peracids as a base, thereby effectively enhancing PO selectivity [18]. Building on these advancements, scientists at the Center for Environmentally Beneficial Catalysis (CEBC) developed a novel catalytic system distinct from traditional TS-1 catalysts. Their CEBC-PO process synergistically combines MTO and PyNO to drive the HPPO reaction. Economic analyses indicate that the CEBC-PO process reduces overall costs by approximately 15% compared to the TS-1-catalyzed HPPO process [14].

The CHPPO process utilizes cumene hydroperoxide (CHP) and propylene as feedstocks. In the presence of TS-1, these reactants undergo epoxidation to produce PO and α,α -dimethylbenzyl alcohol. The latter is then converted back to cumene *via* catalytic hydrogenolysis, and the regenerated cumene is subsequently oxidized with air to re-form CHP, enabling a closed-loop recycling

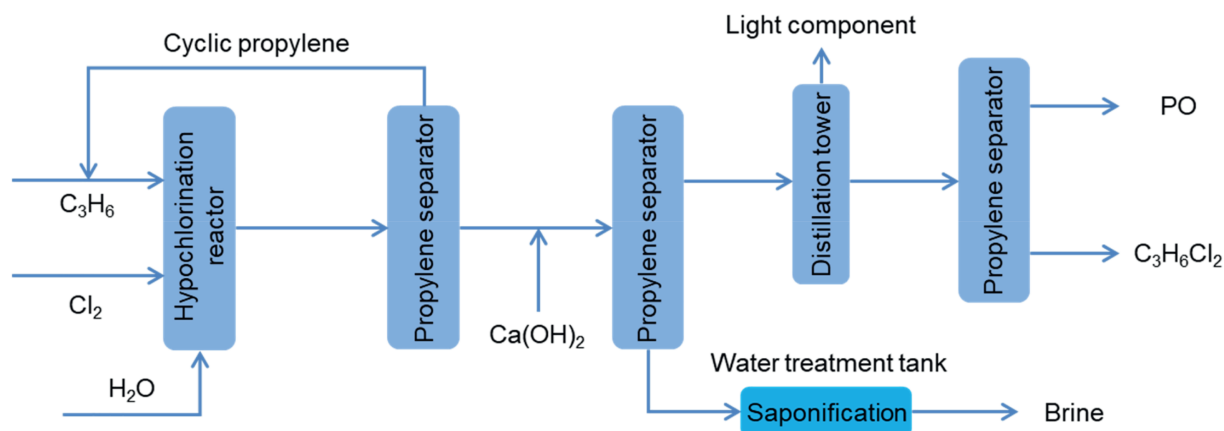


Fig. 3. Schematic diagram of the chlorohydrin process of PO.

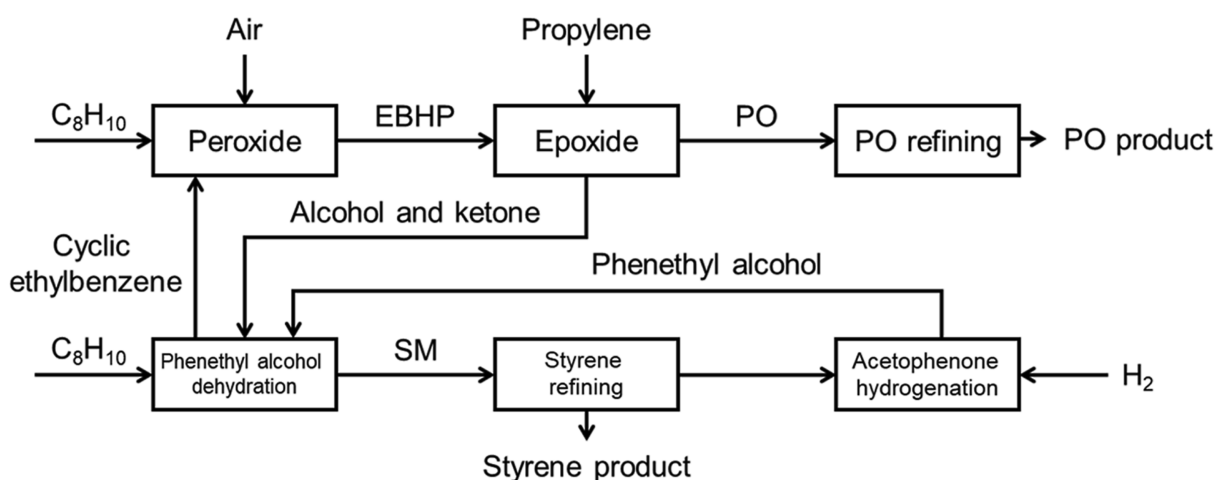


Fig. 4. Schematic diagram of PO/SM cogeneration.

system. In 2003, Sumitomo Chemical Co., Ltd. (Japan) and Lyondell Chemical Company jointly constructed and operationalized a $200000\text{-t}\cdot\text{a}^{-1}$ CHPPO plant in Japan, marking the industrialization of this process.

Direct oxidation methods are characterized by low production costs, minimal environmental impact, and high atom economy. A key advantage is the exclusive production of PO without co-products, which reduces market dependency challenges associated with byproduct management. These benefits have positioned direct oxidation as a focal point for ongoing research. Beyond the commercially mature HPPO and CHPPO processes, two emerging

gas-phase direct oxidation methods are gaining attention: propylene epoxidation with hydrogen–oxygen (using H_2/O_2 mixtures) or with oxygen merely. Both approaches aim to further optimize efficiency and sustainability in PO production.

3. Safety, Environmental, and Lifecycle Risk Analysis

3.1. Substance hazard analysis

Throughout the production of PO, both raw materials and products pose significant risks. Hazardous substances, including

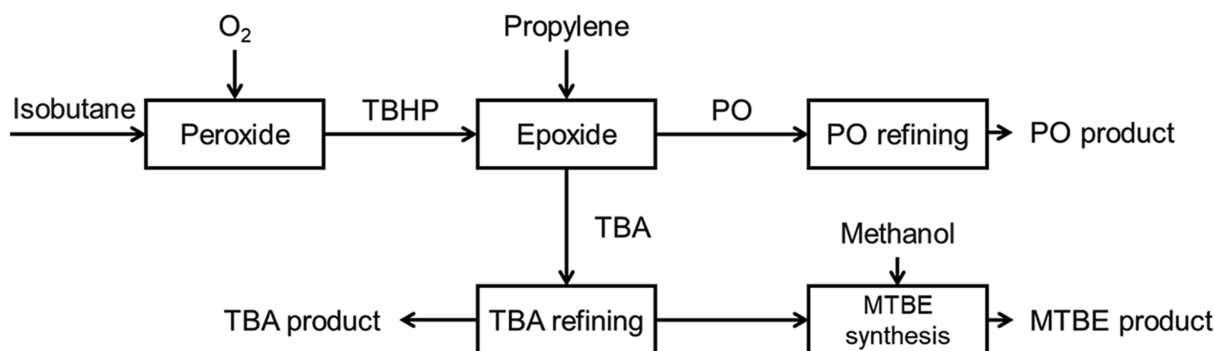


Fig. 5. Schematic diagram of PO/MTBE cogeneration.

propylene, PO, benzene, and chlorine, are listed in China's "List of Hazardous Chemicals" and require strict safety precautions [19]. Materials involved in all major processes—whether the CL process, co-oxidation process, or HPPO process—such as propylene, PO, liquid chlorine, benzene, and H_2O_2 —exhibit inherent danger, including flammability and explosivity. These substances mixed with air form explosive mixtures. For instance, vapors of propylene, propane, and dichloroethane are denser than air, allowing them to spread widely at ground level, where they can ignite upon contact with ignition sources, leading to explosions. Prolonged inhalation of these vapors causes severe health hazards, including poisoning, while their release into water or soil results in persistent environmental contamination. The CL process further introduces environmental risks due to its massive consumption of alkaline agents (e.g., NaOH), which escalates waste treatment costs. In 2015, China's Environmental Protection Bureau imposed administrative penalties on a PO production facility for dust pollution issues at its lime storage yard, highlighting regulatory scrutiny over such hazards.

3.2. Production process risk analysis

PO is prone to polymerization reactions at temperatures above 70°C , which generate localized heat and trigger a self-accelerating cycle of temperature rise, potentially leading to runaway reactions. Therefore, strict temperature control is crucial throughout all processes. In the CL process, the main reaction tower typically operates at $55\text{--}65^\circ\text{C}$ and $0.001\text{--}0.02\text{ MPa}$. For the PO/SM co-oxidation process, reactions occur at $60\text{--}105^\circ\text{C}$ and $0.3\text{--}0.5\text{ MPa}$, where propylene and EBHP undergo multiple steps to produce PO and styrene. However, elevated temperatures in PO/SM co-production units often induce PO polymerization, posing a significant challenge to stable operation [20].

During the chlorohydrination reaction (formation of chloropropane from the reaction of propylene and hypochlorous acid), maintaining an excess of propylene is essential, with a propylene-to-chlorine ratio of $1.1\text{--}1.2$. Excess chlorine can act as an ignition source, posing a risk of combustion incidents. This hazard was documented in small-scale PO production trials in China during the 1960s [21].

While the HPPO process operates under milder conditions ($40\text{--}65^\circ\text{C}$, $0.3\text{--}2\text{ MPa}$), risks escalate during downstream distillation and purification, as shown in Fig. 6 [5]. Partial decomposition of H_2O_2 releases oxygen, which accumulates during flash separation of gaseous propylene. As propylene liquefies, the oxygen concentration in the gas phase increases, potentially

exceeding the explosive limit and triggering combustion or an explosion if exposed to ignition sources [22].

4. Frontiers in Inherent Safety Research for Propylene Oxide Production

4.1. Inherent safety

Contemporary industrial PO production methods present substantial operational risks, with conventional safety protocols typically requiring costly hazard containment infrastructure. In contrast, inherent safety emphasizes eliminating or reducing hazards at their source rather than relying on secondary safeguards to manage consequences—a philosophy first proposed by British safety expert Trevor Kletz in 1977 under the concept of "Inherently Safer Design" [23]. Today, inherent safety in chemical processes involves adopting non-toxic or low-toxicity raw materials, less hazardous technologies, and simplified equipment designs [24].

The fundamental distinction between inherent safety and other safety strategies lies in its proactive elimination of hazards rather than reactive mitigation. Core principles include:

Minimization: reducing the quantity of hazardous chemicals and energy (e.g., via microreactors).

Substitution: replacing hazardous substances or pathways with safer alternatives.

Moderation: operating under milder conditions (e.g., lower temperatures/pressures).

Simplification: streamlining processes to reduce complexity and failure points.

For PO production, these principles manifest as process development prioritizing mild operating parameters, simplified reaction sequences, and reduced hazardous chemical utilization. Below, we explore innovative propylene epoxidation pathways designed under these principles.

4.2. Gas-phase hydrogen–oxygen direct oxidation

In 1988, Haruta's research group [25] first demonstrated that Au/TiO_2 catalysts could selectively catalyze the epoxidation of propylene to PO under a mixed atmosphere of H_2 and O_2 . Since this epoxidation occurs via a heterogeneous gas-phase reaction, the method is termed as the gas-phase hydrogen–oxygen direct oxidation process. Subsequent studies have identified various Au-Ti -based catalysts for this reaction, including TS-1, TS-2, Ti-

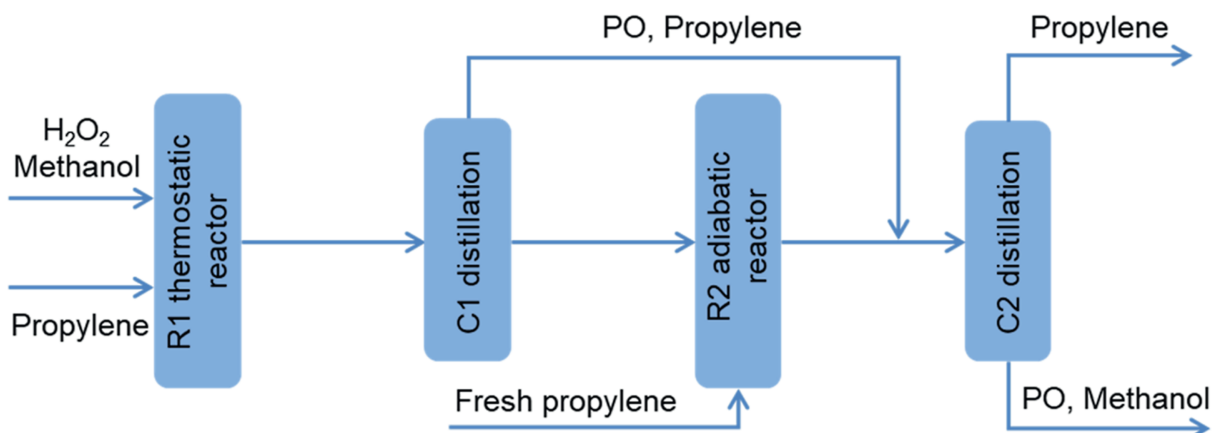


Fig. 6. Schematic diagram of HPPO.

Beta, Ti-MCM-41, Ti-MCM-48, and Ti-SBA-15, with their performance metrics summarized in Table 1 [25–38].

Studies reveal that Ti-containing molecular sieves as support exhibit superior catalytic performance compared to metal oxides. This enhancement is attributed to the ordered pore structure of molecular sieves, which imposes geometric confinement on supported Au nanoparticles, preventing their migration and aggregation [39]. Among these catalysts, Au/TS-1 demonstrates the highest propylene conversion rate, relatively higher PO selectivity and production rate, making it the most industrially viable candidate.

The exceptional performance of Au/TS-1 in gas-phase propylene epoxidation is widely attributed to the synergistic interplay between Au nanoparticles and the TS-1 molecular sieve [40]. The Au active sites catalyze the *in-situ* generation of H_2O_2 from H_2 and O_2 , which subsequently epoxidizes propylene to PO. However, three competing mechanistic pathways dominate current debates: the sequential reaction mechanism, the simultaneous reaction mechanism, and the dinuclear reaction mechanism.

The sequential reaction mechanism posits that H_2O_2 generated by Au catalysis migrates to adjacent Ti defect sites, forming Ti–OOH species, which then act as active sites to catalyze propylene epoxidation to PO [41,42], as illustrated in Fig. 7(a). Haruta *et al.* [43] observed Ti–OOH species on the surface of Au/Ti–SiO₂ catalysts using *in-situ* UV-vis absorption spectroscopy, where an absorption peak at 370 nm indicated charge transfer between –OOH and Ti^{4+} , providing evidence for this mechanism. However, the formation rate of Ti–OOH species was found to be significantly slower than their consumption rate [44], suggesting that H_2O_2 generation is the rate-determining step [45]. The absence of transient kinetic analysis makes it challenging to confirm Ti–OOH as a true intermediate, casting doubt on this mechanism. For instance, Thomson *et al.* [46] calculated energy barriers for Ti–OOH formation at four-coordinated Ti sites near Au nanoparticles (134.3 kJ·mol^{−1}) versus isolated framework Ti sites (70.3 kJ·mol^{−1}), revealing kinetic limitations of the sequential mechanism. The simultaneous reaction mechanism emerged from Delgass *et al.*'s [47,48] determination of reaction orders for H_2 , O_2 , and propylene as 0.60, 0.31, and 0.18, respectively, implying the involvement of at least two active sites. As shown in Fig. 7(b), this mechanism proposes that H_2O_2 generated on Au nanoparticles reacts synchronously with propylene adsorbed on Ti active sites. The rate-determining step involves propylene attacking the H–Au–OOH species to form PO and water. While this pathway requires Au nanoparticles and four-coordinated Ti(IV) sites, the precise structure of these Ti sites remains unresolved despite decades of experimental and computational efforts [49–54]. Copéret *et al.* [6] proposed the dinuclear reaction mechanism, emphasizing the critical role of dinuclear Ti sites rather than isolated framework Ti. Using $H_2^{17}O_2$, they detected solid-state ^{17}O NMR signals

indicative of bridged peroxo bonds at dinuclear Ti sites, as depicted in Fig. 7(c). Density functional theory (DFT) calculations further demonstrated that cooperative effects between two Ti centers decrease the energy barrier for propylene epoxidation.

The gas-phase hydrogen–oxygen direct oxidation process operates under mild reaction conditions with simplified steps, replacing H_2O_2 with H_2 and O_2 as oxidizers. This substitution eliminates the storage, transportation risks, and costs associated with H_2O_2 . Furthermore, its downstream gas separation process avoids the explosion hazards inherent in the flash separation step of the HPPO process [22]. By utilizing less hazardous chemicals and streamlining operations, this method aligns with inherent safety design principles, demonstrating greater potential for intrinsic safety compared to HPPO technology.

Despite its advantages, the gas-phase hydrogen–oxygen process remains in the laboratory research stage, with no industrial-scale adoption to date. However, major corporations such as BASF, Dow Chemical, and Sinopec have actively pursued research and patent filings in this area. To address catalyst performance limitations, BASF and Dow have developed novel catalytic systems and secured related patents. Concurrently, domestic research teams, including Professor Zhou's group [55] at East China University of Science and Technology, have independently designed catalysts tailored for this process. Regarding safety concerns—specifically the explosion risks posed by high concentrations of propylene mixed with H_2/O_2 —the Sinopec Research Institute of Safety Engineering has conducted extensive studies on combustion hazards and proposed explosion suppression and mitigation strategies. Encouraged by promising results from pilot-scale testing, companies like BASF are initiating pilot projects to advance this technology. Industrial implementation is expected to accelerate in the future, offering a new pathway for efficient and inherently safe PO production.

4.3. Microreactors

The microreactor is a continuous-flow reactor with reaction channel dimensions smaller than 1 mm. This design aligns with the minimization principle of inherent safety through three key features: the microreactor's small volume ensures that even in the event of an explosion, the released energy would be less than 1 J; its compact structure enables rapid and precise thermal regulation, significantly reducing the risk of runaway reactions; the reactor's characteristic length is smaller than the mean free path of molecules, preventing flame propagation as energy transfers to the reactor walls instead of between molecules [56]. Kertalli *et al.* [57,58] designed a double-layered packed-bed membrane microreactor coupling two sequential reactions: Pd/SiO₂ catalyzed H_2O_2 synthesis and propylene epoxidation. This system operates under mild conditions (low temperature and

Table 1
Catalytic performance of Au/Ti-containing catalysts on the gas-phase epoxidation of propylene.

Catalyst	Au mass loading/%	Ti/Si (molar ratio)	T/°C	$X_{C_3H_6}/\%$	$S_{PO}/\%$	PO formation rate/g·h ^{−1} ·kg ^{−1}
Au/TiO ₂	0.98	—	50	1.1	>99.0	11.6
Au/Ti–SiO ₂	0.11	—	160	5.4	84.8	120
Au/TiO ₂ –SiO ₂	—	0.01	150	1.5	82.0	—
Au/TS-1	0.05	0.0028	200	8.8	81.0	116
Au/HTS	0.10	0.01	200	—	90.0	150
Au/TS-2	0.09	0.01	200	—	90.0	118
Au/Ti–Beta	8.00	—	250	0.67	0	0
Au/Ti–TUD	2.70	0.03	150	2.1	77.0	29.2
Au/Ti–MCM-41	1.35	0.03	120	0.3	75.0	—
Au/Ti–MCM-48	0.11	0.02	150	5.6	92.0	—
Au/Ti–SBA-15	1.00	0.011	180	1.1	83.7	—
Au/TiO ₂ @SBA-15	0.16	0.013	150	0.1	97.0	—

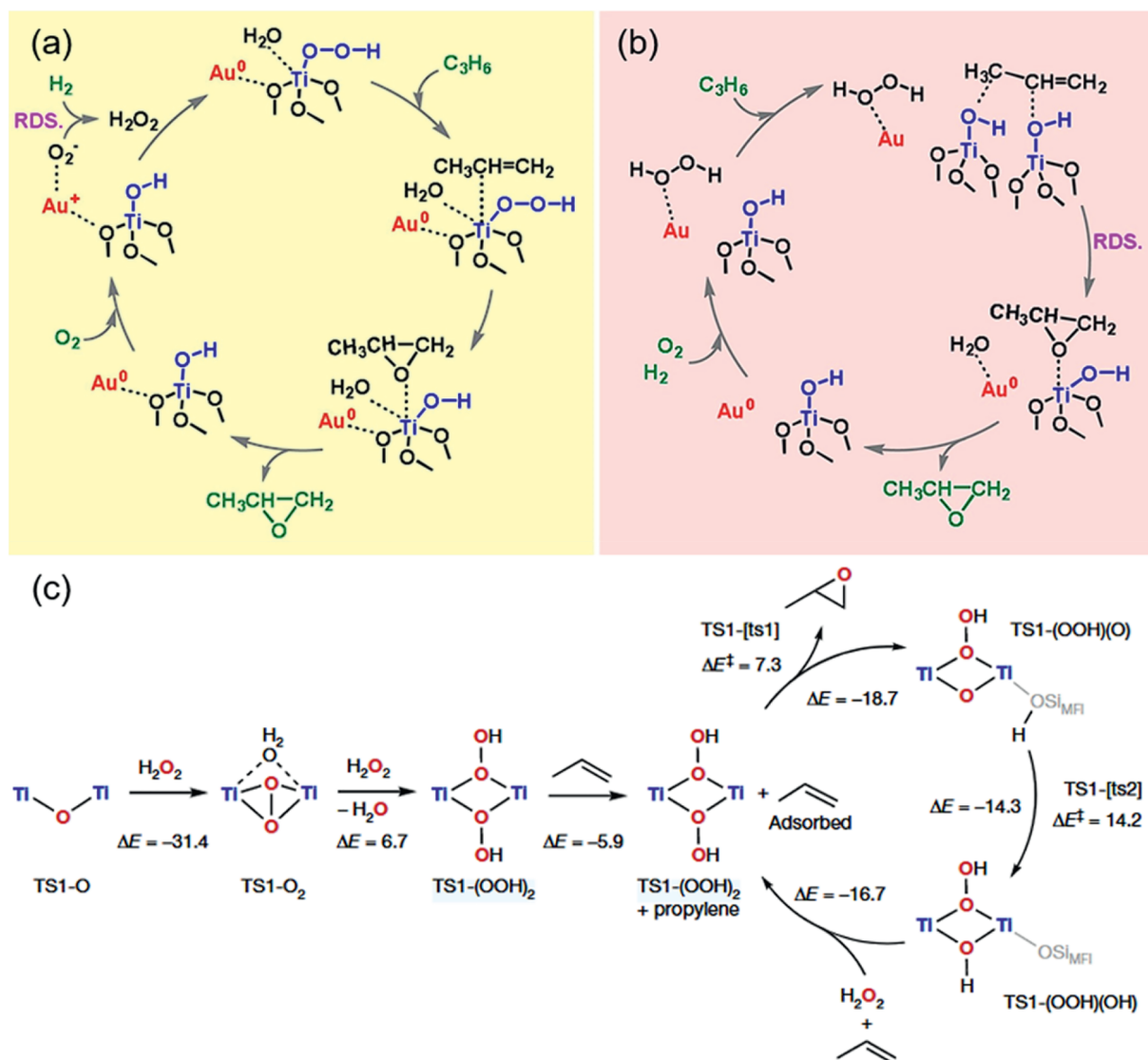


Fig. 7. (a) Sequential reaction mechanism. (b) Simultaneous reaction mechanism. (c) Dinuclear reaction mechanism.

pressure) with reduced hydrogen concentrations, drastically lowering explosion risks. Sasidharan *et al.* [59] employed a hydrothermal method to deposit Au/Ti-1 onto tubular porous α-

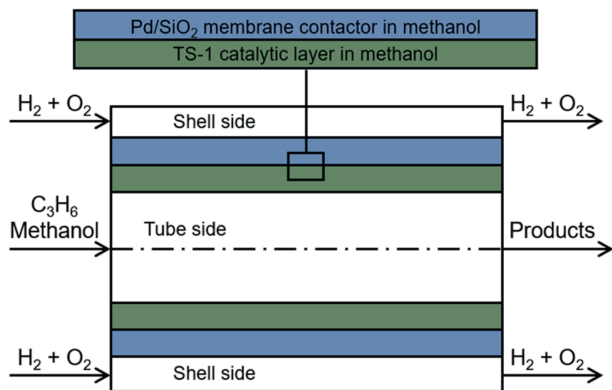


Fig. 8. Double-filled-bed membrane microreactor.

Al₂O₃, forming a catalytic membrane 25–30 μm thick, as shown in Fig. 8. As reactants permeate or diffuse through the membrane, epoxidation occurs at active sites, achieving 80% to 89% PO selectivity. Notably, the reaction temperature was reduced from 180 °C (conventional gas-phase methods) to 130 °C. Aworinde *et al.* [60] developed a mathematical model for optimizing microreactor performance, proposing methods to modulate local oxygen concentration and temperature to enhance epoxidation selectivity. This advancement brings microreactors closer to industrial adoption.

4.4. Electrochemical epoxidation of olefins

Electrochemical processes, leveraging their unique interfacial electron transfer properties, demonstrate exceptional potentials for synthesizing high-value-added and low-carbon-footprint fine chemicals. By enabling precise control over the microenvironment at electrode/electrolyte interfaces, electrochemical systems can steer reactions toward higher atom economy and enhanced inherent safety [61]. Traditional thermal epoxidation processes typically require peroxides as oxidants and stringent temperature

control. In contrast, electrochemical epoxidation driven by renewable electricity offers a greener, more sustainable, and inherently safer pathway.

Electrocatalytic epoxidation is achieved through three primary routes: oxygen-derived hydrogen peroxide pathways, water activation pathways, halide-mediated pathways. Utilizing *in situ* electrochemically generated H_2O_2 via oxygen reduction reactions (ORR), followed by HPPO-like epoxidation. For example, Kwak *et al.* [62] employed Co-based catalysts to produce H_2O_2 *in situ*, which then facilitated olefin epoxidation using TS-1. However, this approach merely couples two independent reactions (ORR and epoxidation), leaving unresolved challenges such as H_2O_2 explosivity. Developing novel routes that use water as the oxygen source to avoid peroxides. Manthiram *et al.* [63] designed an oxidized Pd–Pt catalyst (PdPtO_x/C) that activates water at ambient conditions, achieving a Faradaic efficiency of $66\% \pm 5\%$ for propylene epoxidation at $50 \text{ mA} \cdot \text{cm}^{-2}$ while co-producing high-purity hydrogen. Indirect epoxidation via redox mediators (e.g., Cl^-/Cl_2 , Br^-/Br_2). Sargent *et al.* [64] demonstrated this approach in a flow cell setup, circumventing mass transport limitations at industrial current densities and enabling efficient halide-mediated electro-epoxidation. The primary challenge of electrochemical epoxidation of olefin lies in how to improve the reaction rate and selectivity while achieving process economics and large-scale production. For example, the high cost of precious metals such as Pd and Pt can limit industrial applications; in halide-mediated pathways, while redox mediators like Cl^-/Cl_2 improve reaction kinetics, chlorine species may induce electrode corrosion or side reactions (e.g., organochlorination), compromising equipment lifetime and product purity. However, despite these unresolved challenges, the electrochemical processes overcomes the constraints of traditional thermodynamic limitations and provides new strategies for low-carbon transition and inherent safety of industrial processes.

5. Conclusions

As a pivotal chemical intermediate, PO production processes are evolving toward greater efficiency, safety, and sustainability. Traditional methods face significant challenges: the CL process gradually phases out due to environmental concerns, while the co-oxidation process remains constrained by co-product economics, and even industrialized methods like HPPO grapple with hydrogen peroxide storage/transport risks and costs. The philosophy of inherent safety design has spurred advancements in alternative technologies. Electrochemical epoxidation shows remarkable promise for producing high-value products with a low carbon footprint. However, scaling this process to pilot or industrial levels requires the development of stable and cost-effective mediators, such as non-precious metal catalysts. Microreactors offer safety benefits, but they are hindered by issues such as microchannel clogging, catalyst deactivation, the need for high-precision fabrication for mass production, and difficulties in integrating upstream and downstream processes. Gas-phase hydrogen–oxygen direct oxidation eliminates H_2O_2 logistics risks through H_2/O_2 utilization, simplifies product separation, and reduces combustion hazards. Nevertheless, persistent issues include the sintering of Au nanoparticles and uncertainties regarding the structure of active Ti sites. A primary challenge is to balance the catalytic dependency on TiOH active sites, which are essential for reactivity, with the unintended conversion of PO to propionaldehyde prior to desorption. Tackling these challenges through interdisciplinary research that encompasses catalyst design, reactor engineering, and process

optimization will be crucial for advancing next-generation PO production technologies in line with the goals of green chemistry and industrial safety.

CRediT Authorship Contribution Statement

Hanlin Jin: Writing – review & editing, Writing – original draft, Methodology. Yupeng Tian: Writing – review & editing, Supervision, Resources. Yujia Liu: Writing – review & editing, Validation. Chenyang Zhao: Writing – review & editing, Data curation. Yizhou Yang: Writing – review & editing, Supervision, Resources. Ming Gong: Writing – review & editing, Resources. Xuejing Yang: Writing – review & editing, Supervision, Conceptualization. Bing Sun: Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The author is an Editorial Board Member/Editor-in-Chief/Associate Editor/Guest Editor for this journal and was not involved in the editorial review or the decision to publish this article.

Acknowledgement

Supported by the Open Project of State Key Laboratory of Chemical Safety (SKLCS-2024004).

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