

Research progress on catalyst design and reaction mechanisms for heterogeneous oxygen oxidation of light hydrocarbons

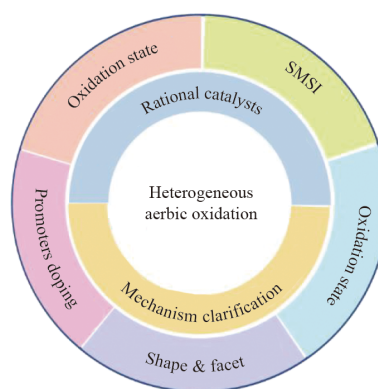
ZENG Zhuang^{1,2}, LI Bin², XIA Changjiu^{1,*}, ZHANG Xiaoxin^{1,*}

¹ State Key Laboratory of Petroleum Molecular and Process Engineering, SINOPEC Research Institute of Petroleum Processing Co., Ltd., Beijing 100083, China;

² Institute of Engineering Technology, SINOPEC Catalyst Co., Ltd., Beijing 100176, China

Abstract: Catalytic oxidation represents a pivotal technology for the valorization of light hydrocarbons, where oxidative dehydrogenation (ODH) and epoxidation reactions using molecular oxygen have garnered substantial interest owing to their high atom economy and environmental friendliness. This review systematically summarizes recent advances in the oxidative dehydrogenation of light alkanes (ethane, propane) and the aerobic epoxidation of light olefins (ethylene, propylene). In terms of rational catalyst design, this review elaborates on performance regulation strategies for metal oxide catalysts such as MoVNbTeO_x mixed oxides, NiO-based, and V-based systems, as well as carbon/boron-based non-metal catalysts in alkane oxidative dehydrogenation, along with silver-based and copper-based catalysts in alkene epoxidation. These strategies include regulating the oxidation state of active sites, strong metal-support interactions, particle size and crystal facet engineering, and promoter modification. At the mechanistic level, combining density functional theory calculations with *in situ* characterization techniques, this review delves into the C–H bond activation and alkene desorption pathways in oxidative dehydrogenation, along with the oxygen insertion routes and competing side reactions in epoxidation. Special attention is given to the dynamic evolution of electrophilic and nucleophilic oxygen species and their decisive role in reaction selectivity. Finally, the review outlines persistent challenges in the field, including suppressing over-oxidation and overcoming the trade-off between conversion and selectivity and proposes future research directions such as the precise design of active centers, development of inherently safer processes, and in-depth analysis of complex reaction networks, aiming to support the green transition of the chemical industry.

Key words: heterogeneous aerobic oxidation; oxidative dehydrogenation; aerobic epoxidation; rational catalyst design; reaction mechanism



C₂–C₄ light olefins are essential feedstocks and platform molecules in the chemical industry, serving as key intermediates for the synthesis of numerous high-value products such as styrene, ethylene glycol, ethylene oxide, polyethylene, polypropylene, propylene oxide, and acrylonitrile^[1–2]. By 2019, global production capacities for ethylene and propylene had reached 207.6 and 110 Mt, respectively^[3]. Conventional production routes—including naphtha steam cracking (SC), fluidized catalytic cracking (FCC), coal-to-olefins *via* methanol (MTO), and Fischer-

Tropsch to olefins (FTO)—share a common limitation: the broad product distribution results in high energy consumption and elevated costs for separation and purification. Driven by growing global demand for light olefins and the increased availability of low-cost C₂–C₄ alkanes from shale gas, alternative pathways such as alkane dehydrogenation have garnered significant interest. Among these, the direct dehydrogenation (DH) has been industrialized but suffers from drawbacks including high reaction temperatures, significant energy consumption, low

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* Corresponding author. E-mail: xiachangjiu.ripp@sinopec.com, zhangxx.ripp@sinopec.com.

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single-pass conversion, and severe catalyst coking^[4]. In contrast, oxidative dehydrogenation (ODH) employs oxidants such as O_2 ^[5-6], CO_2 ^[7-10] or N_2O ^[11] to consume hydrogen *in situ*. Thereby this approach shifts the thermodynamic equilibrium toward higher single-pass conversion while simultaneously suppressing catalyst coking, which is a more energy-efficient and carbon-conscious alternative.

The epoxidation of light olefins constitutes another category of industrially critical oxidation reactions. It aims to selectively convert ethylene, propylene, and other olefins into corresponding epoxides (e.g., ethylene oxide (EO) and propylene oxide (PO)) using oxidants such as H_2O_2 , organic peroxides, or O_2 , which can be further converted to ethylene glycol, ethanolamines, polyether polyols, and other high-value derivatives (Figure 1)^[12].

Nevertheless, the selective ODH of light alkanes remains a significant challenge. Under oxidizing conditions, the resulting olefins are prone to over-oxidation to CO_x . In addition, poor catalytic stability under reaction conditions poses a major obstacle to industrial implementation. Developing highly efficient catalyst systems capable of selectively activating C–H bond while suppressing deep oxidation is crucial for advancing ODH technology. Meanwhile, although ethylene epoxidation to EO has been commercialized, the process generates substantial CO_2 emissions—estimated at approximately 9.3 million tons annually worldwide, accounting for about 0.03% of global carbon emissions^[12]. Enhancing EO selectivity at high ethylene conversion is essential to reducing the carbon footprint and improving process economics. For propylene epoxidation, the HPPO (hydrogen peroxide to propylene oxide) process has advanced considerably, yet it is constrained by the cost and synthesis challenges associated with H_2O_2 . The direct use of molecular O_2 as an oxidant is an attractive alternative, offering 100% atom economy and regarded as a “dream reaction” in heterogeneous catalysis. However, a persistent trade-off between propylene conversion and PO selectivity has limited PO yields to

below 5%, which remains far from commercial viability. Therefore the rational design of catalysts with concurrently high activity and selectivity is imperative.

The oxidative dehydrogenation (ODH) of light alkanes and the epoxidation of light olefins constitute a key technological system for the high-value utilization of light hydrocarbon resources using molecular oxygen (O_2) as a green oxidant. These two processes share substantial commonalities in reaction mechanisms and catalyst design strategies. First, the efficient and selective activation of molecular oxygen is a critical step common to both alkane ODH and olefin epoxidation. The core scientific challenge lies in the precise design of the electronic structure and geometric configuration of catalysts (such as metal oxides, silver, or Cu-based catalysts) to regulate the adsorption and activation pathways of O_2 , thereby selectively generating surface-active oxygen species (e.g., superoxide species O_2^- , lattice oxygen O^{2-} , or peroxide species O_2^{2-}) with tailored reactivity^[13]. The microscopic properties of these active oxygen species (such as electrophilicity/nucleophilicity, redox properties, and migration ability) are the primary factors determining subsequent reaction pathways, as well as the selectivity and yield of the final products. Second, both processes involve the selective catalytic transformation or formation of key chemical bonds (e.g., C–H and C=C), imposing stringent requirements on the “microenvironment” of the catalyst’s active sites. For ODH reactions, the core challenge is how to efficiently cleave the strong and inert sp^3 C–H bonds in alkane molecules while maximally suppressing the cleavage of the more fragile C–C bonds to prevent deep oxidation^[14]. In contrast, epoxidation requires selective activation of the sp^2 C=C bonds in olefins followed by efficient and precise insertion of oxygen atoms, avoiding ring-opening reactions caused by over-oxidation or other side reactions^[15]. Finally, both complex reaction networks face the severe challenge that the target products (olefins or epoxides) are more susceptible to secondary oxidation compared to the starting materials (alkanes or olefins).

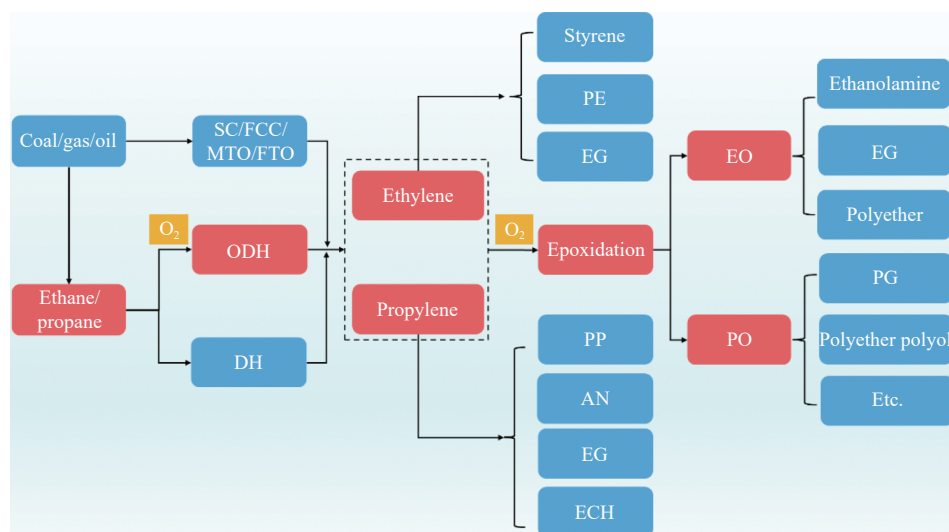


Fig. 1 Schematic illustration of light alkanes conversion to diverse chemicals^[12]

This common dilemma is fundamentally linked to the intrinsic reactivity of active oxygen species on the catalyst surface, their kinetic behavior in surface migration and transfer, and the local concentration at the reaction sites. Therefore, this review juxtaposes these two reaction systems, aiming to conduct a systematic comparison and cross-analysis to elucidate their shared features and distinct characteristics, as well as the underlying principles. This comparative perspective encompasses catalyst design strategies (such as active site structure, promoter modification, and support effects), dynamic structural evolution of active centers during reactions (e.g., valence state changes and dynamic reconstruction), and microscopic reaction mechanisms (e.g., Mars-van Krevelen mechanism, competition between surface reactions and radical pathways). This review perspective not only helps to distill common catalytic principles in the field of heterogeneous selective oxidation, breaking away from the traditional mindset of treating these two processes in isolation, but also holds promise for providing a unified and forward-looking conceptual framework and innovative ideas for the rational design of high-performance catalysts across the entire light hydrocarbon family.

1 ODH of light alkane

1.1 Catalysts for ODH

1.1.1 Catalysts for ODHE

Ethane, the second most abundant component in natural gas and shale gas, is a crucial feedstock for ethylene production. As one of the most important platform molecules in the global petrochemical industry,

approximately 80% of ethylene is utilized in the manufacture of key commercial chemicals, including styrene, vinyl acetate, ethylene oxide, polyethylene, and polyvinyl chloride (PVC)^[16]. Currently, the primary industrial route for ethylene production is steam cracking (SC) of hydrocarbons, achieving an ethane conversion of approximately 60% and an ethylene selectivity of around 85%. While this process operates at extremely high temperatures (800–1000 °C), leading to severe catalyst deactivation due to coke deposition and necessitating frequent regeneration. In contrast, the ethane dehydrogenation pathway, which operates at lower temperatures and offers higher product selectivity, has garnered significant attention and witnessed rapid development in recent years. Compared to ethane direct dehydrogenation (DHE)-a highly endothermic reaction ($\Delta H_{873}^{\circ} = +144.7$ kJ/mol) requiring elevated temperatures (550–700 °C) and exhibiting low per-pass conversion (10%–40%), ethane oxidative dehydrogenation (ODHE) is typically exothermic ($\text{C}_2\text{H}_6 + 0.5\text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$, $\Delta H_{873}^{\circ} = -106.8$ kJ/mol). This thermodynamic profile allows ODHE to proceed at substantially lower reaction temperatures (350–600 °C). However, the key challenges for ODHE lie in suppressing the over-oxidation of ethylene to CO_x and enhancing catalyst stability.

Current ODHE catalysts are primarily divided into two categories: metal-based catalysts (e.g., MoVNbTeO_x mixed oxides and NiO-based catalysts) and non-metal catalysts (e.g., carbon- or boron-based materials). As shown in Table 1 and Figure 2, V-Mo-based catalytic systems, particularly MoVNbTeO_x mixed oxides, represent the most promising system, which can achieve ethylene yields exceeding 60% at around 400 °C, comparable to the conventional steam cracking and demonstrating considerable potential for industrial application.

Table 1 Catalytic performance of the representative catalysts for the ODH of ethane

Catalyst	Reaction conditions	C ₂ H ₆ conversion/%	C ₂ H ₄ selectivity/%	C ₂ H ₄ Yield/%	Ref.
MoVTeNbO _x (M1-stirring)	400 °C, C ₂ H ₆ /O ₂ /He=30:20:50	57.6	90.6	52.2	[17]
MoVTeNbO _x (M1)	400 °C, C ₂ H ₆ /O ₂ /He=30:20:50	58.4	91.2	53.3	[18]
M1/CeO ₂	400 °C, C ₂ H ₆ /O ₂ /He=30:20:50	55.5	90.5	50.2	[18]
M1-1.0	400 °C, C ₂ H ₆ /O ₂ /He=30:20:50	73.0	85.0	62.1	[19]
MoVTeNbCeO-0.1	400 °C, C ₂ H ₆ /O ₂ /(He+N ₂)=10:5:85	56.2	95.4	53.6	[20]
M1@CeO ₂ @Cordierite	400 °C, C ₂ H ₆ /O ₂ /He=30:20:50	60.0	85.0	51.0	[21]
MoVTeNbBiO	400 °C, C ₂ H ₆ /O ₂ /N ₂ =10:10:80	50.0	94.0	47.0	[22]
NiO/Al ₂ O ₃	450 °C, C ₂ H ₆ /O ₂ /N ₂ =10:10:80	59.1	65.3	38.6	[23]
Nb ₂ O ₅ -NiO/Ni-foam	450 °C, C ₂ H ₆ /O ₂ /N ₂ =1:1:8	60.0	68.0	40.8	[24]
Nb-NiO	450 °C, C ₂ H ₆ /O ₂ /He=5:5:90	9.0	84.0	7.6	[25]
o-BCN-1100	500 °C, C ₂ H ₆ /O ₂ /N ₂ =2:1:47	24.5	55.0	13.5	[26]
BNOH	570 °C, C ₂ H ₆ /O ₂ /N ₂ =1:1:4	11	95	10.5	[27]
BNOH	600 °C, C ₂ H ₆ /O ₂ /N ₂ =1:1:4	63.0	80.0	50.4	[27]
s-BN	540 °C, 60 L·g ⁻¹ ·h ⁻¹ , C ₂ H ₆ /O ₂ /He=1:1:48	9.2	100.0	9.2	[28]
s-BN	575 °C, 30 L·g ⁻¹ ·h ⁻¹ , C ₂ H ₆ /O ₂ /He=1:2:47	78.0	60.0	46.8	[28]

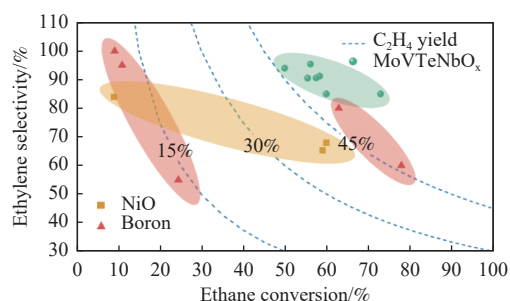


Fig. 2 Correlation between ethane conversion and ethylene selectivity over ODHE

1.1.1.1 MoVNbTeO_x mixed oxides

MoVNbTeO_x catalyst typically consists of M1 and M2 crystalline phases. The former is identified as the active site for the ODHE reaction and its concentration is directly correlated with catalytic performance. The M1 phase possesses an orthorhombic crystal structure, with Te₂M₂₀O₅₇ (M = Mo, V, Nb) as its fundamental structural unit^[29]. Notably, the Te₂M₂₀O₅₇ (001) facet in MoVNbTeO_x exhibits the highest catalytic activity, and surface V⁵⁺ species within the M1 phase are recognized as the active centers responsible for C–H bond cleavage^[30]. Consequently, strategies to enhance the performance of MoVNbTeO_x catalysts focus primarily on three key aspects: (i) synthesizing phase-pure M1 catalysts, (ii) maximizing the exposure of the Te₂M₂₀O₅₇ (001) facet in the M1 phase, and (iii) increasing the surface concentration of V⁵⁺ species in the M1 phase.

Chen et al.^[17] applied mechanical treatment to rod-shaped, phase-pure M1 MoVNbTeO_x catalysts to reduce particle size and preferentially expose the Te₂M₂₀O₅₇ (001) facets. Prolonged mechanical treatment progressively decreased catalyst particle size and increased the exposure of these (001) facets. After 7 d of treatment, the catalyst achieved an ethane conversion of 57.6% with an ethylene selectivity of 90.6% at 440 °C. The corresponding ethylene space-time yield (STY) reached 0.79 g_{C₂H₄}/g_{cat}/h, representing a threefold increase over the untreated catalyst, with stable performance maintained over 200 h. Furthermore, they prepared phase-pure M1 MoVNbTeO_x/CeO₂ nanocomposite catalysts *via* physical mixing or a sol-gel method^[18]. Leveraging the unique redox properties and high oxygen storage capacity of CeO₂, the composite facilitated the oxidation of V⁴⁺ to V⁵⁺ in the M1 phase during catalyst activation, thereby enhancing catalytic performance. The composite catalyst comprising the M1 phase and 4.4 nm CeO₂ nanoparticles exhibited an ethane conversion of 55.5% and an ethylene selectivity of 90.5% at 400 °C, comparable to the phase-pure M1 catalyst. However, the incorporation of low-cost CeO₂ reduced the overall catalyst cost by approximately 20%.

Given the strongly exothermic nature of ODHE, localized “hot spots” can readily form on the catalyst, promoting side reactions and causing sintering. Effective heat removal during the reaction is therefore a critical factor for the

industrial implementation of ODHE. Yan et al.^[31] employed highly thermally conductive structured SiC foam as a support to effectively dissipate the reaction heat, thereby enhancing the stability of the M1 MoVNbTeO_x active phase. This catalyst configuration achieved an ethylene space-time yield of 1.77 g_{C₂H₄}/g_{cat}/h, meeting the performance benchmark required for industrial application.

1.1.1.2 NiO-based catalysts

NiO-based catalysts exhibit notable low-temperature activity for ODHE. However, unsupported or unmodified NiO tends to facilitate the over-oxidation of ethane to CO₂. To mitigate this limitation, strategies such as dispersing NiO on metal oxide supports or incorporating suitable promoters are commonly employed to enhance catalytic performance. Zhang et al.^[23] prepared NiO/Al₂O₃ catalysts using six distinct Al₂O₃ supports with varying specific surface areas and pore volumes. Their study revealed an approximately linear correlation between ethylene yield and the ratio of pore volume to specific surface area of the support. Structural characterization indicated that the physical properties of the Al₂O₃ support critically influence NiO dispersion: supports with smaller pore volumes led to the formation of larger NiO crystallites, whereas those with larger pore volumes promoted a more highly dispersed NiO phase. Zhang et al.^[24] developed a structured catalyst by growing NiC₂O₄ *in situ* on a nickel foam substrate *via* hydrothermal treatment, followed by impregnation with metal salts (M = Li, Mg, Ga, Ce, Zr, Mo, W, Nb) and subsequent calcination to obtain MO_x-NiO/Ni-foam catalysts. Among these, the Nb₂O₅-modified catalyst (Nb₂O₅-NiO/Ni-foam) demonstrated optimal performance, achieving an ethane conversion of 60% and an ethylene selectivity of 68% at 450 °C. Mechanistic studies revealed that an optimal loading of Nb₂O₅ significantly reduces the population of non-selective oxygen species on the catalyst surface, thereby enhancing ethylene selectivity.

1.1.1.3 Non-metal catalysts

Non-metallic materials including carbon nanotubes (CNTs)^[14,32–33], nanodiamonds^[34], boron oxide, and boron nitride^[6,35–36] have demonstrated remarkable performance in the ODH of alkanes, owing to their unique electronic structures and tunable surface properties. For instance, CNTs efficiently activate C–H bonds while suppressing over-oxidation benefiting from their abundant defect sites and adjustable *sp*²/*sp*³ hybridized carbon structures. Nanodiamonds exhibit high thermal stability under severe conditions, attributed to their high specific surface area and stable *sp*³-carbon framework. Furthermore, boron-based catalysts (e.g., hexagonal boron nitride, *h*-BN) promote selective ODH of alkane to olefins owing to their electron-deficient characteristics, which significantly suppresses the formation of CO_x by-products. These metal-free catalysts

not only circumvent issues of metal sintering and coke deposition commonly encountered in metallic systems but also offer advantages in environmental compatibility and cost-effectiveness, thereby opening new avenues for ODH catalysis.

Xin et al.^[26] synthesized nanocarbon (CN) catalysts by pyrolyzing a metal-organic framework (ZIF-8) at high temperatures (900–1100 °C), followed by boron (B) doping and oxidative modification *via* hydrothermal treatment. The optimized *o*-BCN-1100 catalyst exhibited high activity and stability, achieving an ethylene yield of 13.5%. Shi et al.^[27] employed hydroxyl-functionalized boron nitride (BNOH) as a catalyst for ODHE, achieving 95% ethylene selectivity at an ethane conversion of 11%, and maintaining 80% selectivity even at 63% conversion, performance comparable to that of industrial steam cracking. The catalyst demonstrated stable performance over 200 h of testing. Mechanistic investigations revealed that hydrogen abstraction of B–OH groups by molecular oxygen dynamically generates active sites and initiates ethane dehydrogenation. Further work by Huang et al.^[28] showed that high-surface-area BN nanosheets also exhibited high selectivity in ODHE. The catalyst achieved nearly 100% ethylene selectivity at 10% conversion and maintained 60% selectivity even at a high conversion of 78%, with stable operation for over 400 h. Operando infrared spectroscopy and ¹⁸O isotope tracer study confirmed that B–O(H) active sites were formed preferentially at the BN edges under ethane-assisted conditions, with oxygen atoms from O₂

replenishing these B–O sites to complete the catalytic cycle.

1.1.2 Catalysts for ODHP

By 2021, the global annual production capacity of propane dehydrogenation units had exceeded 10 million metric tons, and this figure is projected to exceed 15 million metric tons by 2025. Compared to ethane, the propane possesses a lower C–C bond dissociation energy (376 vs. 359 kJ/mol), which makes its oxidative dehydrogenation of propane (ODHP) more susceptible to over-oxidation to CO₂, consequently lowering propylene selectivity and overall yield. As summarized in Table 2, the propylene yield in current ODHP processes is generally below 40%. Therefore, the main challenge for ODHP technology lies in developing catalyst systems that can efficiently and selectively activate the C–H bonds in propane while minimizing C–C bond cleavage and secondary oxidation of the produced propylene. Catalyst systems for ODHP are broadly categorized into metal-based and non-metal-based catalysts. Metal-based catalysts primarily include vanadium-based, nickel/molybdenum-based and cobalt-based systems, while non-metal catalysts mainly include boron-based and carbon-based materials^[37–38]. In vanadium-based catalysts, activity and selectivity are strongly dependent on the polymerization state of surface vanadyl (V⁵⁺=O) species.

Table 2 Brief summary of the catalytic performance of the representative catalysts for the ODH of propane

Catalyst	Reaction conditions	C ₃ H ₈ conversion/%	C ₃ H ₆ selectivity/%	C ₃ H ₆ Yield/%	Ref.
3%V- <i>m</i> -SiO ₂	500 °C, C ₃ H ₈ /O ₂ =1:1	19.8	66.7	13.2	[44]
V ₂ O ₅ /KIT-6	600 °C, C ₃ H ₈ /O ₂ /N ₂ =1:1:8	55.0	64.7	35.6	[45]
VO _x /La ₂ O ₃ -Al ₂ O ₃	525 °C	25.0	80.0	20.0	[46]
Mo ₁ V _{0.5} Al _{0.02} K _{0.03} O _x	300 °C, C ₃ H ₈ /O ₂ =8:1	12.7	83.2	10.6	[47]
α-Mg ₂ V ₂ O ₇	520 °C, C ₃ H ₈ /O ₂ /N ₂ =6:1:10	2.4	96.4	2.3	[48]
CA-P	400 °C, C ₃ H ₈ /O ₂ /He=1:1:4	27.9	36.0	10.0	[41]
Co ₃ O ₄	100 °C, C ₃ H ₈ /O ₂ /He=1:19:80	0.8	100.0	0.8	[49]
Co-AIM(MOFs)	230 °C, C ₃ H ₈ /O ₂ =3:5	7.5	24.0	1.8	[50]
NiMoO ₄	560 °C, C ₃ H ₈ /O ₂ /N ₂ =15:15:70	15.0	66.2	9.9	[42]
Meso-NiMoO ₄	475 °C, C ₃ H ₈ /O ₂ /N ₂ =10:12.5:77.5	18.2	63.9	11.6	[51]
Mesoporous NiO	450 °C, C ₃ H ₈ /O ₂ /He=1.2:1:1.2	25.8	51.3	13.2	[52]
NiO-POM	450 °C, C ₃ H ₈ /O ₂ /He=4:16:80	23.0	65.0	15.0	[53]
CMK-3	600 °C, C ₃ H ₈ /O ₂ /He=2:1:27	57.6	47.3	27.2	[54]
B _x CN	350 °C, C ₃ H ₈ /O ₂ /He=2:2:9	7.5	81.3	6.1	[55]
<i>h</i> -BN	490 °C, C ₃ H ₈ /O ₂ =2:1	14.0	79.0	11.1	[43]
BNNTs	490 °C, C ₃ H ₈ /O ₂ =2:1	8.2	77.0	6.3	[43]
Ni@BO _x /BN	440 °C, C ₃ H ₈ /O ₂ /N ₂ =1:1.5:3.5	25.0	68.0	17.0	[56]
BO _x /Ni/BN	440 °C, C ₃ H ₈ /O ₂ /N ₂ =1:1.5:3.5	22.5	71.2	16.0	[5]
BO _x /Ni-Rh/BN(15:1)	440 °C, C ₃ H ₈ /O ₂ /N ₂ =1:1.5:3.5	26.7	69.9	18.7	[5]

Isolated $V^{5+}=O$ sites are considered crucial for the selective activation of C–H bonds, as their moderate electrophilicity allows them to attack C–H bonds in propane while causing minimal C–C bond cleavage. In contrast, highly polymerized V–O–V structures exhibit excessive acidity, which promotes deep oxidation of propylene^[39]. Thus, controlling the dispersion of vanadium species *via* supports (e.g., SiO_2 , Al_2O_3 , ZrO_2) is a key strategy for achieving high selectivity^[40]. For cobalt-based and nickel/molybdenum-based catalysts, the challenge lies in tuning the strength of the metal-oxygen (M–O) bond. If the M–O bond is too strong, lattice oxygen reactivity is insufficient, leading to low catalyst activity; if too weak, the lattice oxygen becomes overly active and tends to trigger deep oxidation. In cobalt-based catalysts, modulating the Co^{3+}/Co^{2+} ratio is a common approach to regulate selectivity^[41]. For nickel/molybdenum-based systems, the formation of specific metalates (e.g., $NiMoO_4$) is employed to optimize redox properties^[42].

Boron-based catalysts, particularly hexagonal boron nitride (*h*-BN), are believed to have active sites located at edge or defective B–O sites^[43]. Their high selectivity originates from a unique activation mechanism: B–O sites can abstract hydrogen atoms from propane with a low energy barrier to form olefins, while the surface lacks sites that efficiently activate O_2 to generate highly reactive electrophilic oxygen species, thereby fundamentally suppressing the deep oxidation pathway of propylene. Carbon-based catalysts (e.g., nanodiamond, carbon nanotubes) typically rely on surface oxygen-containing functional groups such as carbonyls as active sites. Their selectivity strongly depends on the type of oxygen species (nucleophilic or electrophilic)^[44]. Surface modification with heteroatoms (e.g., N, P) can promote the formation of nucleophilic oxygen species. However, the main challenge for carbon materials lies in the dynamic evolution of their surface chemical environment under reaction conditions, which often leads to a decline in activity and selectivity over time.

1.1.2.1 Vanadium-based catalysts

Supported vanadium-based catalysts represent one of the earliest and most effective catalytic systems for ODHP^[57], with the highest reported propylene yields approaching 35%. Research on these catalysts primarily focuses on improving vanadium dispersion, modulating metal-support interactions, tuning catalyst acidity/basicity, and optimizing vanadium speciation and valence states^[58].

Enhancing vanadium dispersion. Maximizing the dispersion of vanadium species exposes more active sites for oxidative dehydrogenation, thereby improving catalytic performance. The use of supports with high surface area and well-developed porosity, such as mesoporous SiO_2 ^[44–45,59–60] and Al_2O_3 ^[46], is generally considered beneficial. Liu et al.^[45] synthesized a series of V-KIT-6

catalysts with varying vanadium loadings encapsulated within three-dimensional ordered mesoporous silica *via* hydrothermal method. Vanadium existed as tetrahedrally coordinated V^{4+} , tetrahedrally coordinated V^{5+} , and octahedrally coordinated V^{5+} . By adjusting the pH during synthesis, both the catalyst structure and vanadium content could be controlled. Under optimized conditions at 600 °C with a $C_3H_8/O_2/N_2$ volumetric ratio of 1:1:8, the 5V-KIT-6 catalyst achieved a propane conversion of 55.0%, with propylene selectivity and yield reaching 64.7% and 35.6%, respectively, significantly outperforming catalysts prepared by conventional impregnation. This enhancement was attributed to highly dispersed active sites and the favorable mass transport provided by the three-dimensional ordered pore system of the KIT-6 support.

Modulating metal-support interactions. Tailoring the strong metal-support interactions (SMSI) has proven to be an effective strategy for modifying catalytic performance^[61]. Jiang et al.^[62] demonstrated that loading 0.5% vanadium oxide species onto high-surface-area hexagonal boron nitride (*h*-BN) led to the formation of B–O–V linkages, effectively anchoring sub-nanometer (single atoms or clusters) VO_x species on the *h*-BN surface. Compared to the bare support, the VO_x -loaded catalyst doubled the yield of C_2 – C_3 olefins in ODHP. Chen et al.^[63] utilized vanadium-titanium interactions to construct highly dispersed monolayer or sub-monolayer VO_x nanostructures on a TiO_2 support. This catalyst exhibited exceptional ODHP performance, achieving over 90% propylene selectivity at 500 °C with a turnover frequency (TOF) of $1.9 \times 10^{-2} s^{-1}$, which is more than 20 times higher than that of conventional bulk V_2O_5 catalysts.

Tuning catalyst acidity and basicity. The acid-base properties of catalysts significantly influence ODHP performance. Acidic sites facilitate alkane activation; however, excessively strong acidity promotes deep oxidation and lowers olefin selectivity. In contrast, basic sites are generally more favorable for selective olefin formation^[64–65]. Modifying these properties can be achieved by selecting supports with tailored acid-base characteristics or introducing additives such as rare-earth oxides (e.g., La_2O_3 ^[46]), alkali metals (e.g., K ^[47]), or alkaline earth metals (e.g., Mg ^[48]). Dinse et al.^[66] investigated the influence of acid strength for supported vanadium catalysts using different carriers (Al_2O_3 , TiO_2 , CeO_2 , SiO_2 , ZrO_2). They found the acid strength followed the order $V-ZrO_2 > V-TiO_2 > V-Al_2O_3$, which inversely correlated with propylene selectivity, suggesting that strong acid sites facilitate deep oxidation of propylene. Lemonidou et al.^[64] examined the effect of alkali metals (Li, Na, K) on the structure and performance of V_2O_5/Al_2O_3 catalysts. The addition of alkali metals reduced catalytic activity but markedly enhanced propylene selectivity, with the enhancement scaling with the alkali ionic radius. This improvement is attributed to two factors: i) alkali metals neutralize non-selective strong acid sites, inhibiting over-oxidation to CO_2 , and ii) they promote rapid desorption of propylene molecules,

preventing secondary reactions.

Optimizing vanadium speciation and valence states. The chemical environment and valence state of vanadium species are another crucial factor. Zhang et al.^[48] compared three crystalline phases (MgV_2O_6 , $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$, $\text{Mg}_3\text{V}_2\text{O}_8$) in the Mg–V–O system and found that $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$, which features corner-sharing V–O–V structures, was most favorable for propylene formation, whereas $\text{Mg}_3\text{V}_2\text{O}_8$ with isolated VO_4 tetrahedra exhibited moderate performance. Although MgV_2O_6 showed the highest activity, its selectivity was relatively poor. The role of vanadium valence states remains debated. Liu et al.^[67] achieved tunable control over the $\text{V}^{5+}/\text{V}^{4+}/\text{V}^{3+}$ ratio by varying the vanadium surface density on alumina and observed a positive correlation between catalyst turnover frequency (TOF) and V^{3+} content, suggesting that V^{3+} species may serve as the primary active sites for propane dehydrogenation.

1.1.2.2 Cobalt-based catalysts

Cobalt-based catalysts have attracted attention in ODHP due to their notable low-temperature C–H bond activation capability and tunable redox properties. Davies et al.^[68] demonstrated that Co_3O_4 nanocrystals can activate propane at room temperature with 100% initial propylene selectivity. Although the propane conversion was very low, this represented the first observation of room-temperature propane activation, providing valuable insights for mechanistic studies. Huang et al.^[41] prepared Co–Al layered double oxides (LDOs) by calcining Co–Al layered double hydroxides (LDHs) intercalated with different anions (NO_3^- , SO_4^{2-} , PO_4^{3-} , CO_3^{2-}). Characterization revealed that Co species primarily existed as Co^{2+} and Co^{3+} within a Co_2AlO_x spinel structure. Catalysts derived from SO_4^{2-} and PO_4^{3-} intercalated LDHs, benefiting from strong host-guest interactions and higher CoO_x dispersion, showed significantly superior propylene selectivity compared to those from NO_3^- and CO_3^{2-} precursors, as the latter anions decompose readily during calcination.

Despite their unique low-temperature activity, current Co-based catalysts typically exhibit propylene yields below 10%, substantially lower than vanadium-based systems and far from industrial requirements. Further advances in active site engineering are crucial to improving both propane activation capacity and propylene selectivity.

1.1.2.3 Nickel/molybdenum-based catalysts

Nickel/molybdenum-based catalysts represent another early-stage catalytic system applied to the oxidative dehydrogenation of light alkanes, typically employing molybdenum oxide, nickel oxide, or nickel molybdate as

active components. A primary limitation of these catalysts is their relatively low activity for propane dehydrogenation, generally resulting in propylene yields below 15%. Current research focuses on heteroatom doping^[42], modulation of active site valence states^[69] and crystal phases^[70], and optimization of pore structure^[51–52].

Stern et al.^[42] investigated the effect of different transition metals in AMoO_4 ($\text{A} = \text{Ni, Co, Mg, Mn, Zn}$) molybdate catalysts. All transition metal molybdates exhibited ODH activity, with NiMoO_4 demonstrating the best performance, achieving 7% propane conversion and 85.2% propylene selectivity at 560 °C. Other approaches to enhance Ni–Mo catalyst performance include pore structure engineering and modulation of Mo^{5+} valence states. For instance, Farin et al.^[51] synthesized mesoporous $\beta\text{-NiMoO}_4$ using a self-assembling copolymer template under mild calcination temperatures (350–450 °C), which exhibited a sixfold increase in propylene yield compared to conventional non-porous NiMoO_4 .

1.1.2.4 Carbon-based catalysts

The active sites for ODH on carbon materials are nucleophilic oxygen species, such as ketonic ($\text{C}=\text{O}$) or carbonyl groups, which can attack the C–H bonds of alkanes to form olefins while being simultaneously reduced to hydroxyl groups (Figure 3)^[14]. The hydroxyl groups are subsequently re-oxidized to carbonyl groups by O_2 , completing the catalytic cycle^[14,33]. In contrast, electrophilic oxygen species (e.g., peroxy, superoxy, carboxyl groups) on carbon surfaces are considered responsible for complete oxidation, as they attack electron-rich $\text{C}=\text{C}$ bonds to form CO_x . Therefore, tuning the type and concentration of surface oxygen species is critical for regulating selectivity. Common strategies to achieve this include pre-treatment modification and heteroatom doping (e.g., N, B, P).

Frank et al.^[33] demonstrated that heteroatom doping with boron (B) or phosphorus (P) significantly enhanced the propylene selectivity of oxidized carbon nanotubes (oCNTs). The optimal 5B-oCNT catalyst achieved 70% propylene selectivity at 4.5% propane conversion and maintained stable performance for 200 h at 400 °C. Characterization indicated that the incorporated boron oxide (BO_x) species weakened propane adsorption, favoring propylene formation. Sun et al.^[34] further modified nanodiamond surfaces with boron oxide, and observed a volcanic trend in propylene selectivity with increasing boron loading. At low loadings, B species coordinated with surface defects via O–H bonds to form tricoordinated BO_3 species that suppressed the formation of electrophilic oxygen and enhanced propylene selectivity. Higher boron loadings led to the formation of tetracoordinated BO_4 species linked to carbonyl oxygen atoms, which covered the active $\text{C}=\text{O}$ sites and degrading catalytic performance.

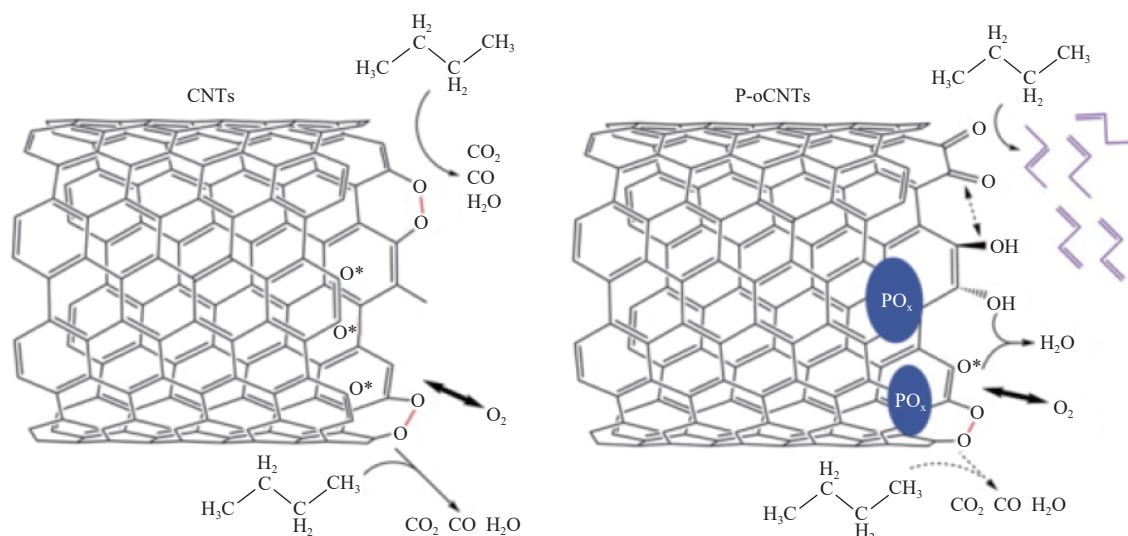


Fig. 3 The oxidative dehydrogenation of propane over CNTs and P-modified oCNTs^[14]
(with permission from AAAS)

1.1.2.5 Boron-based catalysts

Beyond carbon materials, boron-based catalysts such as boron nitride and boron oxide demonstrate distinctive advantages in ODHP. Grant et al.^[43] first applied hexagonal boron nitride (*h*-BN) and boron nitride nanotubes (BNNTs) to ODHP, which exhibited exceptionally high olefin selectivity. Specifically, *h*-BN achieved 79% propylene selectivity at 14% propane conversion, with total olefin selectivity exceeding 90%, and maintained stability for over 30 hours. The reaction mechanism on *h*-BN differed from that on conventional V-based catalysts: O₂ initially adsorbs to form a peroxo-like B–O–O–N structure, which cleaves the C–H bond of propane to generate a propyl radical, subsequently converting to propylene.

Modifying the chemical environment of boron by supporting metal atoms on BN substrates can further enhance ODHP performance. Gao et al.^[56] constructed a Ni@BO_x/BN core-shell structure by supporting Ni on BN followed by calcination under CO₂. This catalyst exhibited a 93-fold increase in surface-specific activity compared to pristine *h*-BN and demonstrated excellent low-temperature performance. Mechanistic studies revealed that the sub-surface Ni atoms strongly interacted with oxygen atoms in the surface BO_x layer, lowering the energy barrier for radical initiation and optimizing the kinetic balance between BO–H bond cleavage and B–OH regeneration.

1.2 Reaction mechanisms in ODH

A widely recognized framework for the reaction mechanisms in oxidative dehydrogenation (ODH) of light alkanes has established. On reducible metal oxide catalysts (e.g., VO_x, CoO_x, MoO_x), the reaction predominantly follows the Mars-van Krevelen (MvK) mechanism—a redox process mediated by lattice oxygen. In contrast, on surfaces lacking lattice oxygen, such as hexagonal boron nitride (*h*-

BN) and carbon-based materials, a radical pathway predominates.

Taking the oxidative dehydrogenation of propane as an example, the catalytic cycle *via* the lattice oxygen mechanism (MvK mechanism) comprises two key steps (Figure 4). First, a propane molecule interacts with lattice oxygen (O²⁻) on the metal oxide surface, which leads to C–H bond activation, generating a propyl radical and a surface hydroxyl group. The propyl radical subsequently undergoes dehydrogenation to form propylene and water, simultaneously creating an oxygen vacancy on the catalyst surface. Second, gaseous O₂ adsorbs and dissociates, replenishing the surface oxygen vacancy and regenerating the lattice oxygen species, thereby completing the catalytic cycle. A defining characteristic of this mechanism is that propane activation is directly accomplished by the lattice oxygen, rather than *via* gaseous oxygen molecules.

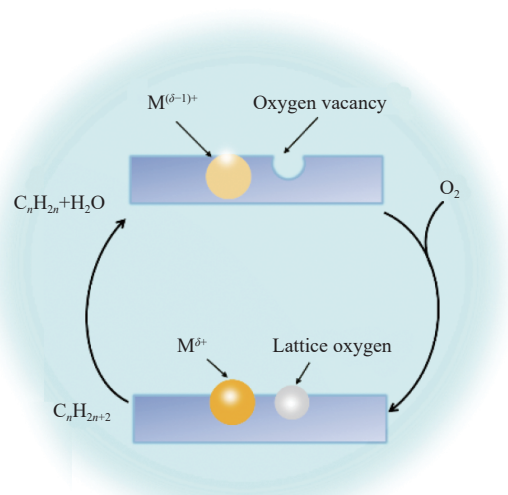


Fig. 4 Schematic illustration of the Mars-van-Krevelen mechanism for ODH on reducible metal oxides

The radical mechanism is centered on the formation of propyl radicals ($\cdot\text{C}_3\text{H}_7$) and hydroperoxyl ($\cdot\text{OOH}$) radicals. Using the reaction pathway for propane ODH on boron-based catalysts as an illustrative example: the initial step involves the cleavage of a methylene C–H bond in an adsorbed propane molecule, generating an adsorbed propyl species and a boron hydroxyl group (B–OH). Subsequently, gaseous O_2 adsorbs on the catalyst surface and reacts with a hydrogen atom from the boron hydroxyl group, forming a $\cdot\text{OOH}$ radical and a boron-oxygen (B–O $\cdot$) radical. This B–O $\cdot$ radical then reacts with another adsorbed propane molecule (C_3H_8^*) or a peroxide intermediate, regenerating the boron hydroxyl group and producing a gaseous propyl radical ($\cdot\text{C}_3\text{H}_7$). Finally, the propyl radical ($\cdot\text{C}_3\text{H}_7$) undergoes dehydrogenation to yield propylene and a hydrogen peroxide (H_2O_2) intermediate, thereby completing one catalytic cycle^[56].

1.3 Processes Innovations in ODH

In addition to catalyst development and mechanistic understanding, significant progress has also been achieved in recent years regarding the reaction processes for oxidative dehydrogenation of alkanes. To further address the challenges of selectivity control and safety risks associated with co-feeding alkanes and oxygen, chemical looping oxidative dehydrogenation (CL-ODH) technology has emerged as a promising alternative^[71]. Based on the Mars-van Krevelen mechanism, this technology employs redox-active metal oxides (e.g., FeO_x , MoO_x , MnO_x , etc.) as oxygen carriers to decouple the reaction into two separate stages: alkane dehydrogenation and oxygen carrier regeneration (Figure 5). This approach fundamentally prevents direct contact between hydrocarbons and gaseous oxygen, significantly enhancing process safety and suppressing deep oxidation side reactions. The core of CL-ODH technology lies in the development of high-performance oxygen carriers and their integration with reactor systems^[72].

In 2016, Neal et al.^[73] first applied CL-ODH to ethane oxidative dehydrogenation, using Na- and W-promoted Mn/SiO₂ and Mn/MgO as oxygen carriers, achieving satisfactory activity, ethylene selectivity, and redox stability of the carriers. Since then, research on oxygen carriers for oxidative dehydrogenation of alkanes has developed rapidly, yielding a series of important achievements. For instance, Wang et al.^[74] developed a $\text{MoO}_3\text{-Fe}_2\text{O}_3$ oxygen carrier that achieved 49% propane conversion and 90% propylene selectivity in CL-ODH, while maintaining structural stability and performance without degradation over nearly 300 redox cycles, demonstrating promising potential for industrial application.

Additionally, to lower oxygen concentration in the reaction system, suppress over-oxidation, and enhance process safety, membrane reactors have been applied to ODH reactions.

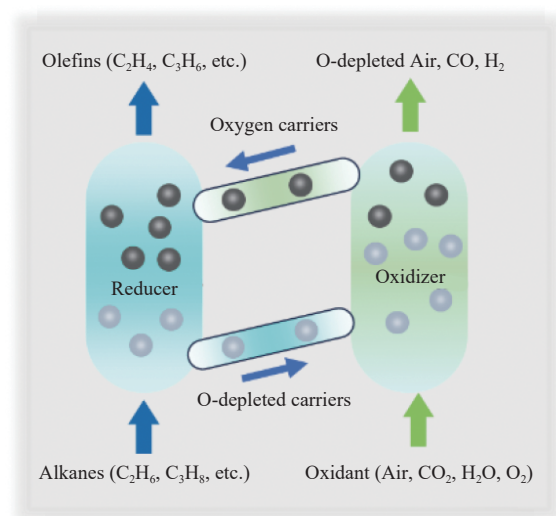


Fig. 5 The graphic scheme of chemical looping processes for ODH of alkane

By enabling a more controlled and uniform distribution of oxygen, these reactors can significantly improve propylene yield. Particularly, oxygen-selective mixed ionic-electronic conducting perovskite membrane reactors have demonstrated excellent performance in propane oxidative dehydrogenation^[75–76]. For example, Jin et al.^[76] investigated the diffusion behavior of oxygen and its effect on reaction performance in a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ hollow fiber membrane reactor. Theoretical simulations revealed that even at a high temperature of 1000 °C, the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ hollow fiber membrane maintained excellent selectivity for O^{2-} ion transport. At a propane conversion of 58%, the propylene selectivity reached as high as 91%. This finding provides valuable insight and a useful reference for researchers aiming to overcome the trade-off between activity and selectivity in ODH reactions.

2 Epoxidation of light olefins

2.1 Catalysts for epoxidation of light olefins

2.1.1 Catalysts for direct epoxidation of ethylene

Epoxides, featuring highly strained three-membered oxirane rings, exhibit remarkable chemical reactivity and serve as pivotal platform molecules for producing a wide range of value-added chemicals. By 2020, global annual demand for ethylene oxide (EO) had reached approximately 35 million tons, growing steadily at 5%–7% per year. The global market for EO and its derivatives was valued at nearly US\$45 billion and is projected to reach US\$65 billion by 2027^[77]. The selective oxidation of ethylene to ethylene oxide (EO) represents one of the most successful catalytic processes in the history of the chemical industry. The silver catalyst supported on $\alpha\text{-Al}_2\text{O}_3$ ($\text{Ag}/\alpha\text{-Al}_2\text{O}_3$) is the only catalytic system that has been commercialized on a large scale^[15], with key technologies licensed by companies

such as Shell, Scientific Design (SD), and Sinopec. For unmodified Ag/ α -Al₂O₃ catalysts, the EO selectivity is constrained by ethylene conversion (Figure 6). At ethylene conversions ranging from 4% to 8%, the EO selectivity remains approximately 50%. Through the addition of promoters such as Cl, Cs, Re, Mn, Mo and S, the EO selectivity can be significantly increased to around 90%, albeit maintaining the per-pass ethylene conversion at a level of 10%–15%^[15,78]. CO₂ is one of the primary byproducts in the ethylene epoxidation reaction. Statistics show that the global annual CO₂ emissions resulting from the ethylene oxide process reach as high as 9.3 million tons, accounting for 0.03% of global carbon emissions^[12] and 5% of the total carbon emissions from chemical production^[79]. Therefore, further improving the selectivity of ethylene oxide while suppressing CO₂ generation under high ethylene conversion conditions is essential for enhancing process economics and reducing carbon emissions. The catalytic performance in ethylene epoxidation is strongly influenced by the microstructure of supported Ag nanoparticles, including particle size, oxidation state, morphology, and exposed crystal facets, as well as promoter modifications and strong metal–support interactions (SMSI). This section reviews recent progress in silver-based epoxidation catalysts, with emphasis on the aforementioned aspects.

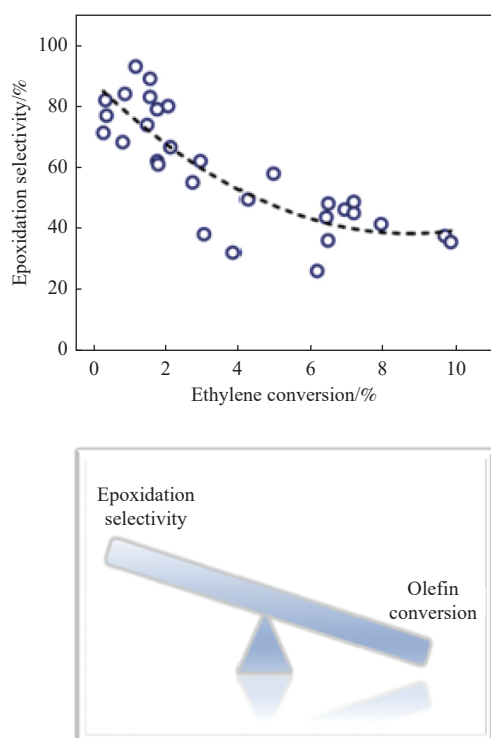


Fig. 6 Trade-off between the epoxidation selectivity and ethylene conversion on unpromoted Ag based catalysts^[80] (with permission from ACS Publications)

2.1.1.1 Particle size effects

For structure-sensitive reactions such as ethylene

epoxidation, the dimensions of the active Ag nanoparticles critically determine both catalytic activity and product selectivity. Lamoth et al.^[81] summarized the reported correlation between catalytic performance and Ag particle size across various studies. A general trend shows that ethylene oxide selectivity first increases and then declines as the particle size grows from below 10 nm to nearly 100 nm, with an optimum typically observed at moderate sizes around 100–150 nm. For instance, Iyer et al.^[82] prepared a series of silver catalysts with particle sizes ranging from 5 to 400 nm and found that both small (5–50 nm) and large (>250 nm) Ag nanoparticles gave lower EO selectivity, while particles in the 130–150 nm range yielded the highest selectivity. In contrast, the relationship between ethylene conversion and Ag particle size remains debated. Van den Reijen et al.^[83] reported a positive volcanic trend, where ethylene conversion increased as particle size grew from 20 to 70 nm, then decreased with further size increase up to 400 nm. Conversely, Van Hoof et al.^[84] observed a gradual decline in conversion with increasing particle size up to 50 nm, beyond which it plateaued.

2.1.1.2 Oxidation state

The catalytic performance is directly correlated with the oxidation state of silver, with substantial evidence suggesting that partially oxidized Ag^{δ+} species exhibit higher epoxidation activity compared to metallic Ag⁰. Pu et al.^[12] employed EDS mapping to monitor the catalyst surface under reaction conditions, revealing that fresh Ag particles showed negligible surface oxidation, while exposure to reactants led to the formation of a partially oxidized surface layer. Operando Raman spectroscopy combined with DFT calculations further demonstrated that the reconstructed and partially oxidized AgO_x surface was more stable than the metallic Ag surface under reaction conditions. Chen et al.^[85] utilized operando Raman spectroscopy and transient kinetic measurements to show that a sufficiently oxidized AgO_x surface layer increased the concentration of peroxide ($\cdot\text{O}_2^-$) intermediates, thereby promoting ethylene activation and enhancing EO selectivity.

2.1.1.3 Crystal facet effects

Precise control of exposed crystal facets through nanoarchitecture of catalyst morphology offers a powerful strategy for tuning catalytic performance^[86]. Two key challenges in facet engineering are: i) elucidating the relative efficacy of different facets—such as Ag(111), Ag(110), Ag(100) and Ag(211) for ethylene epoxidation, and ii) developing synthesis strategies that preferentially expose the most active facets. Christopher et al.^[87] modulated both the exposed facets and catalytic performance by controlling Ag nanoparticle shape. They

found that Ag nanowires predominantly exposed the highly active Ag(100) facet, whereas supported Ag/ α -Al₂O₃ favored the thermodynamically stable Ag(111) facet. Correspondingly, Ag nanowires achieved 60% EO selectivity, significantly higher than that of 45% obtained with Ag/ α -Al₂O₃. DFT calculations revealed that on the Ag(100) surface, the energy barrier for converting the oxametallacycle (OMC) intermediate to acetaldehyde (1.02 eV) is higher than that for its conversion to EO (0.92 eV), favoring EO formation. In contrast, on Ag(111), the activation barriers for these two pathways are nearly identical (0.75 vs. 0.73 eV), leading to comparable formation of both EO and acetaldehyde, and the latter is more susceptible to further oxidation, ultimately resulting in CO₂ formation.

2.1.1.4 Promoter effects

In ethylene epoxidation, metal promoters enhance EO selectivity by tuning the oxophilicity of active sites. For example, cesium, copper, and cobalt can reconstruct catalytic sites, facilitating oxygen binding to the promoter and ethylene adsorption on silver, thereby lowering the activation barrier for EO formation^[88]. DFT calculations suggest that promoters adjust the oxygen adsorption energy (ΔG_{O^*}), balancing activity and selectivity and overcoming the inherent trade-off observed in unpromoted silver catalysts. Moreover, co-doping with elements such as cesium and rhenium exhibits synergistic effects, further enhancing EO selectivity beyond the level attainable with single promoters. Chen et al.^[89] employed machine learning-assisted first-principles simulations to deeply analyze the synergistic effect between Re and Cs. When only Re promoter (in the form of ReO₄) is present, it excessively enhances the electrophilicity of the active Ag surface, thereby promoting the isomerization of ethylene oxide (EO) to acetaldehyde. Conversely, Cs alone facilitates the formation of strongly nucleophilic surface O* species, which accelerates the combustion of ethylene to CO₂. Only when ReO₄ and Cs act together does the catalyst surface achieve charge balance, thereby maximizing EO selectivity.

2.1.1.5 Metal-support Interactions

The surface area, acidity/basicity, and surface functional groups of the support directly influence ethylene epoxidation performance. Industrially, low surface area, weakly acidic α -Al₂O₃ is preferred because it stabilizes Ag nanoparticles while suppressing EO isomerization and over-oxidation mediated by surface hydroxyl groups (OH*). Van den Reijen et al.^[90] passivated a SiO₂ support to remove surface OH* groups, reducing the rate of EO secondary reactions by 94% and achieving performance superior to conventional α -Al₂O₃. Yang et al.^[91] demonstrated that an Al-modified MnO₂ supported Ag catalyst (Ag/Al-MnO₂) effectively modulated the electronic state of Ag 3d orbitals. This catalyst achieved 90% EO selectivity at 170 °C, with acetaldehyde as the sole by-product and no detectable CO₂ formation. XPS characterization indicated that the active sites consist primarily of partially oxidized Ag^{δ+} species stabilized by metal-support electronic interactions, ensuring rapid formation of intermediates and desorption of EO. Recently, He et al.^[92] showed that etching α -Al₂O₃ with NH₄F solution increased its internal surface roughness. After loading with Cs- and Re-promoted Ag, the resulting catalyst (100Ag/0.24Cs/0.33Re) exhibited high stability and an EO selectivity of 84.2%.

2.1.2 Catalysts for direct epoxidation of propylene

Global demand for propylene oxide (PO) is projected to exceed 20 million tons by 2025, with a total market value surpassing US\$15 billion^[93]. Since the initial development of propylene epoxidation processes by Shell and Dow Chemical in the 1940 s, it has undergone multiple evolutionary stages from the chlorohydrin process to the co-oxidation method, and subsequently to direct oxidation routes (Figure 7), progressively advancing toward higher atom economy and improved environmental sustainability^[94]. Currently, third-generation direct oxidation technologies, aligned with green chemistry principles, represent the dominant research focus and industrial frontier.

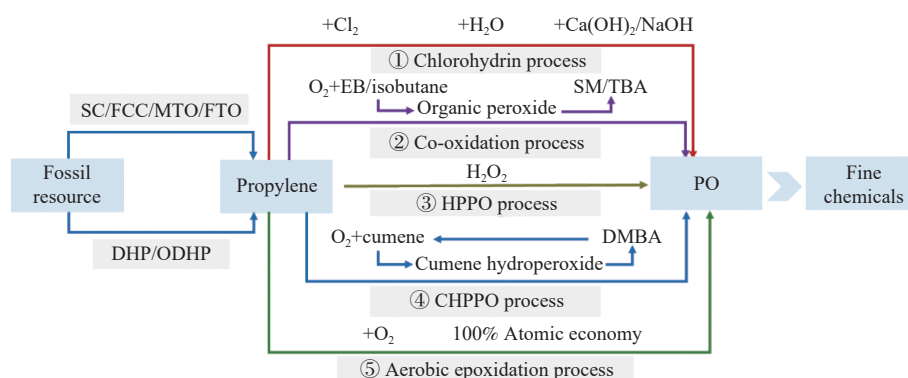


Fig. 7 Evolution of process for PO production from propylene

Among these, the hydrogen peroxide to propylene oxide (HPPO) process, which employs TS-1 zeolite catalysts, achieves PO selectivity exceeding 90% with water as the only by-product, representing an environmentally friendly route. However, its commercial viability is constrained by the high cost of the H_2O_2 oxidant^[95].

The use of molecular oxygen (O_2) as an oxidant is regarded as the most attractive alternative for PO synthesis, offering 100% atom economy. Nevertheless, current catalytic systems suffer from unacceptably low PO yields, rendering them commercially unviable. The development of high-performance catalysts and compatible reaction engineering thus remains the key challenge for realizing direct epoxidation of propylene with O_2 .

Currently, catalysts employed for the direct epoxidation of propylene with oxygen primarily comprise Group IB metals and their oxides, including Cu ^[96–97], Ag ^[13,98] and Au ^[99–100]. Table 3 presents representative catalytic performances in propylene epoxidation, copper-based catalysts are the most extensively studied system, demonstrating the highest performance and showing the greatest application potential among these metals. Nevertheless, the propylene oxide (PO) yield remains generally below 2%, indicating substantial room for improvement in catalytic efficiency. In addition, metal-zeolite composite materials have recently exhibited

remarkable performance in the direct oxidation of propylene, with certain catalysts achieving PO yields exceeding 20%.

2.1.2.1 Copper-based catalysts

In contrast to silver catalysts, which predominantly remain in the metallic state, copper-based catalysts typically form copper oxide species (Cu_2O and CuO) under typical direct propylene epoxidation conditions. Substantial evidence suggests that Cu^+ sites in Cu_2O serve as the key active centers for propylene epoxidation. Current strategies to enhance the performance of CuO_x -based catalysts primarily focus on four aspects: engineering strong metal-support interactions (SMSI), controlling morphology and crystal facet, leveraging size effects, and incorporating promoter modification. Lü et al.^[97] supported copper on a TiO_2 carrier calcined at ultra-high temperature and observed that, due to strong metal-support interactions, Cu predominantly existed as ~3 nm nanopatches anchored at Lewis acid sites on the support surface. *In situ* characterization identified these Lewis acid sites as penta-coordinated Ti^{4+} cations associated with tri-coordinated O^{2-} anions (denoted as L_β sites).

Table 3 Comparison of various catalysts for propylene aerobic epoxidation

Catalyst	Reaction conditions	C_3H_6 conversion/%	PO selectivity/%	PO yield/%	PO formation rate/($\text{mmol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$)	Ref.
Cu/SiO_2	225 °C, 0.1 MPa, 50 mL/min	0.25	53	0.13	0.014	[101]
$\text{K}^+ - \text{CuO}_x/\text{SBA-15}$	350 °C, 0.1 MPa, 60 mL/min	12	15	1.80	2.1	[102]
$\text{K}^+ - \text{CuO}_x/\text{SBA-15}$	250 °C, 0.1 MPa, 60 mL/min	0.95	46	0.44	0.51	[102]
$\text{KAc-Cu}/\text{SiO}_2$	250 °C, 0.1 MPa, 50 mL/min	1.3	61	0.79	0.14	[103]
Dodecahedra Cu_2O	250 °C, 0.1 MPa, 50 mL/min	0.8	13	0.10	0.057	[104]
Cubic Cu_2O	225 °C, 0.1 MPa, 50 mL/min	0.8	10	0.08	0.044	[104]
c- Cu_2O -27	90 °C, 0.1 MPa, 50 mL/min	0.04	79	0.03	–	[105]
c- Cu_2O -27	110 °C, 0.1 MPa, 50 mL/min	0.06	82	0.05	–	[105]
s- Cu_2O -NF	150 °C, 0.1 MPa, 30 mL/min	0.03	100	0.03	0.08	[96]
s- Cu_2O -NF	175 °C, 0.1 MPa, 30 mL/min	0.15	84	0.13	0.18	[96]
s- Cu_2O -NF	225 °C, 0.1 MPa, 30 mL/min	1.25	30	0.38	0.83	[96]
$\text{VCe}_{0.2}\text{Cu}_{0.8} - \text{NaCl}(20)$	250 °C, 0.1 MPa	0.19	43.4	0.08	0.165	[106]
$\text{Cl-RD-Cu}_2\text{O}$	200 °C, 0.1 MPa, 50 mL/min	1.0	63	0.63	0.5	[107]
$\text{Cl-RD-Cu}_2\text{O}$	150 °C, 0.1 MPa, 50 mL/min	0.05	>95	0.05	0.038	[107]
$\text{Au}/\text{TS-1-K1}$	200 °C, 0.1 MPa, 20 mL/min	0.88	52	0.46	0.19	[108]
$\text{Ag-MoO}_3/\text{ZrO}_2$	350 °C, 0.1 MPa, 62.6 mL/min	0.6	58	0.35	0.236	[109]
$\text{NaCl-Ag-MoO}_3/\text{ZrO}_2$	400 °C, 0.1 MPa, 62.5 mL/min	2.0	63	1.26	–	[110]
Ag-CaCO_3	220 °C, 0.3 MPa, 30 mL/min	10	5	0.50	–	[111]
NaCl-Ag-CaCO_3	260 °C, 0.3 MPa, 30 mL/min	3	45	1.67	1.24	[112]
Co@Y	500 °C, 0.1 MPa, 60 mL/min	24.6	57	14.02	4.72	[113]
Ti-Beta-3%	560 °C, 0.1 MPa, 60 mL/min	25.0	90	22.50	14	[94]
Ti-Beta-4%	560 °C, 0.1 MPa, 60 mL/min	33.1	78	25.82	15.6	[94]

This Cu/TiO₂ catalyst exhibited high activity in direct propylene epoxidation, achieving a maximum PO space-time yield of 44 mmol/(g·h). The PO yield correlated directly with the consumption of Lewis acid sites, indicating that the interaction between Cu and these sites is critical for PO formation. DFT calculations further revealed that the Cu⁺ species located at the Ti-O-Cu interface, formed specifically on the L_β sites, function as the active sites for propylene epoxidation.

The exposed facets of Cu₂O strongly influence both the configuration of adsorbed oxygen and the resulting PO selectivity. By synthesizing Cu₂O nanocrystals with controlled morphologies, specific crystal facets can be preferentially exposed, thereby enhancing PO selectivity. Hua et al.^[104] prepared Cu₂O nanocrystals with different shapes to selectively expose distinct facets: octahedra predominantly exposed (111) facets, rhombic dodecahedra exposed (110) facets, and cubes primarily exposed (100) facets (Figure 8)^[104]. Combined characterization and DFT calculations indicated that one-coordinate Cu sites on Cu₂O(111), three-coordinate O sites on Cu₂O(110), and two-coordinate O sites on Cu₂O (100) serve as active centers for acrolein, PO and CO₂ formation, respectively. The Cu₂O(110) facet was found to yield the highest PO selectivity, reaching 20%. Subsequently, Xiong et al.^[105] synthesized cubic Cu₂O nanocrystals with different particle sizes (27, 106, 774 nm), all predominantly exposing (100) facets with edges corresponding to (110). Among them, the c-Cu₂O-27 catalyst (27 nm) exhibited the best performance, achieving over 80% PO selectivity at 90–110 °C. This was attributed to the higher relative proportion of (110) edges in smaller cubes, whereas larger particles were dominated by (100) terraces. Recently, Qiu et al.^[96] synthesized hollow Cu₂O nanoframes using ligand-protection and selective facet-etching technique. This structure not only increased the specific surface area but also selectively preserved the active Cu₂O(110) facets, simultaneously enhancing activity, selectivity, and stability. At 175 °C, the catalyst achieved a PO yield of 0.18 mmol/(g·h) with 83.8% selectivity and maintained stable performance for 300 min.

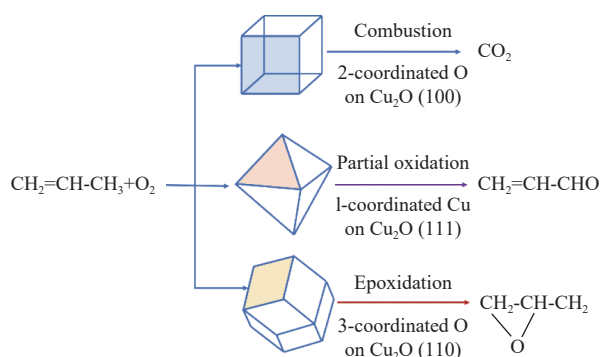


Fig. 8 Crystal plane controlled selectivity of Cu₂O catalysts in the oxidation of propylene with molecular oxygen^[104]

Wang et al.^[114] investigated the direct epoxidation of propylene over SBA-15-supported copper catalysts (1% Cu

loading) containing both Cu₂O and CuO active phases, modified with different alkali metals. Alkali metal promotion reduced activity but increased PO selectivity, following the order: Li < Na < K < Rb < Cs. Potassium modification delivered the highest PO yield of 14%. Characterization revealed that K⁺ incorporation reduced both the strength and number of acid sites on the catalyst, thereby suppressing PO isomerization and over-oxidation to CO_x. Zhan et al.^[107] demonstrated that incorporating Cl into the Cu₂O lattice enhanced both conversion and PO selectivity in propylene epoxidation while preventing Cl leaching. Chlorine-doped rhombic dodecahedral Cu₂O (mainly exposing (110) facets) achieved 63% PO selectivity with a turnover frequency (TOF) of 12.0 h⁻¹ at 200 °C, outperforming most metal catalysts under mild conditions. Characterization and theoretical calculations revealed that Cl-modified Cu(I) sites facilitated the formation of electrophilic oxygen species, thereby promoting PO formation.

2.1.2.2 Group IB noble metal catalysts

In addition to copper-based systems, supported silver and gold catalysts have also demonstrated promising performance in propylene epoxidation. Carbonio et al.^[13] showed that introducing oxyanions (e.g., SO₄²⁻, PO₄³⁻) to enrich electrophilic oxygen species on silver catalysts could enhance PO selectivity. Furthermore, they found that the addition of Cl to SO₄²⁻-modified Ag catalysts further activated the oxyanions, increasing PO selectivity by approximately fourfold. Yu et al.^[98] developed a series of SBA-15-encapsulated Ni@Ag core-shell nanoparticles. The optimal Ni₁Ag_{0.4}/SBA-15 catalyst achieved a PO selectivity of 70.7% at 220 °C and atmospheric pressure, which was attributed to lattice strain in the Ag shell induced by the Ni core. Wang et al.^[99] investigated the synergy between Au nanoparticles (Au NPs) and Au single atom catalysts (Au SACs). In gas-phase propylene epoxidation, Au NPs provided unique sites for H₂/O₂ and propylene activation, generating hydroperoxyl species that restored the activity of poisoned Au single-atom sites. Remarkably, the addition of Au NPs amounting to only 0.3% of the Au SACs increased the PO formation rate and selectivity by 56-fold and 3-fold, respectively, while maintaining stability for over 150 h.

2.1.2.3 Metal-zeolite composite systems

Li et al.^[113] reported that faujasite zeolite-encapsulated Co ions (Co@Y) exhibited outstanding high-temperature activity in direct propylene epoxidation. At 500 °C, the catalyst achieved 24.6% propylene conversion with 57% PO selectivity, corresponding to a PO space-time yield of 4.72 mmol/(g·h), and maintained stable performance for 200 h. Spectroscopic characterization revealed that molecular oxygen was initially activated on isolated Co^{δ+} sites, which subsequently reacted with propylene to form PO, while the Co sites underwent a redox cycle between

Co^{2+} and $\text{Co}^{\delta+}$ ($2 < \delta < 3$). More recently, Li et al.^[94] demonstrated that Ti-Beta zeolites containing isolated framework Ti species efficiently catalyze propylene epoxidation. At 560 °C, the catalyst achieved 25% propylene conversion with 90% PO selectivity, yielding a record PO formation rate of 14 mmol/(g·h), approaching that of industrial ethylene oxide processes. Mechanism studies indicated that H-terminated penta-coordinated Ti species in Beta zeolite frameworks served as the active sites, with lattice oxygen in Ti–OH groups initiating the epoxidation. This finding illuminates a promising pathway toward the industrial implementation of the direct propylene epoxidation using O_2 .

2.2 Reaction mechanisms of olefin aerobic epoxidation

2.2.1 Mechanism of ethylene epoxidation

The epoxidation of ethylene is generally understood to proceed *via* two potential mechanistic pathways: the atomic oxygen mechanism and the oxametallacycle (OMC) intermediate mechanism. In the atomic oxygen mechanism, adsorbed oxygen atoms exist in two distinct forms: nucleophilic and electrophilic. Electrophilic oxygen species, which possess relatively low electron density (often described as “weakly adsorbed oxygen”), preferentially

attack the electron-rich π -bond of ethylene, leading to ethylene oxide (EO) formation. In contrast, nucleophilic oxygen atoms tend to react with the electron-deficient C–H bonds of ethylene, resulting in complete combustion to CO_2 and H_2O ^[15]. The OMC intermediate mechanism proposes that O_2 first adsorbs and dissociates on Ag sites, forming Ag–O bonds. Subsequently, the C=C double bond of ethylene adsorbs on an adjacent Ag site and reacts with the oxygen atom, forming a cyclic oxametallacycle (OMC) intermediate (Figure 9)^[115]. This OMC intermediate can either desorb and cyclize to form EO or undergo hydrogen transfer to form acetaldehyde, which is then readily combusted to CO_2 and H_2O ^[116].

2.2.2 Mechanism of propylene epoxidation

The reaction pathway for propylene epoxidation primarily follows either the Mars-van Krevelen (MvK; lattice oxygen) mechanism or the Langmuir-Hinshelwood (LH; adsorbed oxygen) mechanism^[105], with the operative pathway being dictated by the structure of the active site. As illustrated in Figure 10(a)^[105], the LH mechanism initiates with the co-adsorption of C_3H_6 and O_2 , leading to the formation of a metal-bound peroxo intermediate (OOMP, e.g., $\text{Cu-O-O-CH}_2\text{-CH}(\text{CH}_3)\text{-Cu}$). This OOMP intermediate then dissociates to release one molecule of PO, leaving an atomic oxygen species behind.

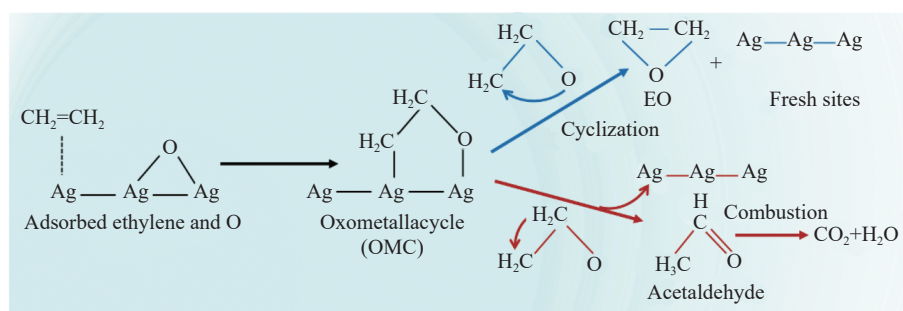


Fig. 9 Suggested mechanism of ethylene epoxidation on silver catalysts through the oxometallacycle (OMC) intermediate^[115]

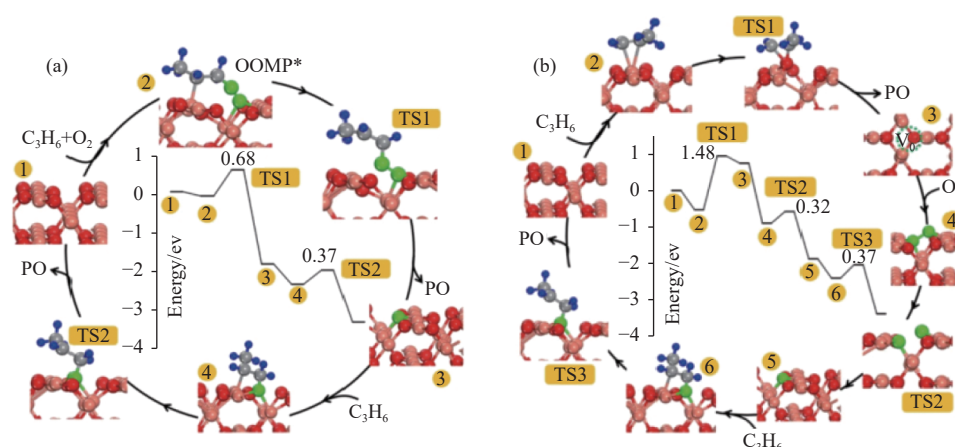


Fig. 10 Energy profile and catalytic cycle along with the optimized structures of intermediates and transition states for propylene epoxidation on $\text{Cu}_2\text{O}(110)$ *via* (a) LH and (b) MvK mechanisms^[105] (with permission from Springer Nature)

Finally, this atomic oxygen reacts with another adsorbed propylene molecule ($\text{C}_3\text{H}_6(\text{a})\text{-Cu}$) to form a second PO molecule, thereby completing the catalytic cycle. As shown in Figure 10(b), the MvK mechanism begins with the reaction of adsorbed propylene ($\text{C}_3\text{H}_6(\text{a})\text{-Cu}$) with a surface lattice oxygen atom, generating one PO molecule and creating a surface oxygen vacancy (V_O). Subsequently, an O_2 molecule adsorbs and dissociates at the vacancy, replenishing the lattice oxygen and generating an additional active oxygen species. This oxygen species then reacts with another adsorbed propylene molecule to form a second PO, thereby closing the catalytic cycle.

3 Conclusion and outlook

This review summarizes recent advances in the full-chain conversion of light alkanes to olefins and epoxides using molecular oxygen, with a focus on catalyst design and reaction mechanisms. Key common principles and system-specific challenges are highlighted.

A universal principle for active-site regulation involves inhibiting highly reactive sites through geometric isolation or electronic effects. This approach is key to overcoming the conversion-selectivity trade-off, whether in suppressing olefin over-oxidation or preventing epoxide ring-opening. Second, precise control of active oxygen species is essential for achieving high selectivity. High selectivity in oxidative dehydrogenation relies on nucleophilic oxygen (e.g., lattice oxygen), whereas efficient epoxidation requires electrophilic oxygen species (e.g., atomic oxygen) for targeted olefin oxidation. Finally, recognizing the dynamic evolution of catalysts under operating reaction conditions is critical. Surface reconstruction, valence cycling, and oxygen vacancy formation collectively determine the true activity and stability of catalysts. This necessitates a shift in characterization techniques from static analysis to dynamic resolution.

In ODH, the ethane route (using MoVNbTeO_x catalysts) approaches industrial viability with ~60% ethylene yield. However, the propane route faces challenges due to C–C bond cleavage, limiting yields to <40%. Advances require precise tuning of vanadium-based catalysts (dispersion, valence states) or carbon/boron-based catalysts (surface chemistry, B–O coordination). For ethylene epoxidation, silver catalysts are being optimized through control of size, facet, and promoter, but suppressing CO_2 remains a major challenge. In direct propylene epoxidation with O_2 , copper-based and other systems still show low propylene oxide yields (<5%), with the central challenge being the activity-selectivity trade-off for industrialization.

To overcome current selectivity and safety challenges, future research should focus on: (1) Precision catalyst design to establish precise structure-performance relationships at the atomic and electronic levels, with emphasis on single-atom/full-site catalysts, synergistic dual active sites, as well as machine learning-assisted design.

(2) Inherently safe processes to fundamentally avoid explosion risks and enhance process efficiency, *via* novel reaction engineering strategies including chemical looping oxidative dehydrogenation (CL-ODH), membrane reactor technology, and distributed oxygen feeding/staged feeding processes. (3) Integrated research approaches such as combining high spatiotemporal resolution characterization with quantitative kinetic analysis to deepen the understanding of catalytic processes and support the development of next-generation high-efficiency catalysts.

Through interdisciplinary collaboration and technological innovation, molecular oxygen-mediated green oxidation processes hold promise for enabling the high-value conversion of light hydrocarbons in the context of the “Dual Carbon” goals.

Declaration of Competing Interest

The authors declare no conflict of interest.

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非均相低碳烃氧气氧化催化剂设计与反应机理研究进展

曾 壮^{1,2}, 李 斌², 夏长久^{1,*}, 张晓昕^{1,*}

(1. 中石化石油化工科学研究院有限公司 石油化工分子转化与反应工程全国重点实验室, 北京 100083;

2. 中国石化催化剂有限公司工程技术研究院, 北京 100176)

摘 要: 催化氧化是实现低碳烃高值化利用的关键技术, 其中, 氧气参与的氧化脱氢和环氧化反应因其原子经济性高、环境友好的特点而备受关注。本工作综述了低碳烷烃(乙烷、丙烷)氧化脱氢、低碳烯烃(乙烯、丙烯)环氧化的研究进展。在催化剂理性设计方面, 重点阐述了烷烃氧化脱氢中所涉及的 MoVNbTeO_x 复合氧化物、NiO 基、V 基等金属氧化物以及碳/硼基非金属催化剂以及烯烃环氧化中银基与 Cu 基催化剂的性能调控策略, 包括调控活性位点氧化态、金属-载体强相互作用、粒径与晶面工程以及助剂改性等。在反应机理层面, 结合密度泛函理论计算与原位表征技术, 深入剖析了氧化脱氢过程中 C-H 键的活化与烯烃脱附机制, 以及环氧化反应中氧原子对 C=C 键的插入路径与竞争副反应, 揭示了亲电性与亲核性活性物种的动态演变规律及其对反应选择性的决定性作用。本综述指出该领域仍面临抑制过度氧化、打破转化率与选择性间的“Trade-off”效应等挑战, 并对未来发展方向进行展望, 包括活性中心的精准设计、本质安全工艺的开发以及复杂反应网络的深入解析, 以期为化工过程的绿色升级提供参考。

关键词: 非均相氧气氧化; 氧化脱氢; 环氧化; 催化剂理性设计; 反应机理

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作者简介:



曾壮(1993), 博士, 高级工程师, 主要从事分子筛合成与应用、烷烃氧化脱氢和烃类选择性氧化、苯/苯酚羟基化反应研究, t-zengzhuang.ripp@sinopec.com。



张晓昕(1971), 博士, 正高级工程师。主要从事化工领域催化材料和反应工程研究。针对己内酰胺、十二内酰胺、己二胺和过氧化氢合成过程进行加氢催化剂、分子筛催化剂和相关工程的基础和应用研究, zhangxx.ripp@sinopec.com。



夏长久(1984), 博士, 研究员, 博士生导师。主要从事分子筛合成与绿色催化氧化工艺开发, 开展杂原子分子筛金属活性中心状态与晶内孔道结构调变研究, 开发以双氧水和氧气为氧化剂的绿色高效有机物氧化新工艺, xiachangjiu.ripp@sinopec.com。