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Abstract: Feedstock valorisation with preformed H$_2$O$_2$ in conjunction with titanosilicate zeotypes is particularly attractive due to the increased selectivity, lower operating temperatures and improved process efficiency (particularly lower energy usage and enhanced atom economy) compared to aerobic pathways or alternative stoichiometric oxidants. However, numerous environmental and financial concerns associated with the application of commercial H$_2$O$_2$ remain. These concerns have led to a growing interest in the application of the in-situ synthesized oxidant for a range of chemical transformations. Herein, we provide an overview of the key contributions to this emerging field of oxidative catalysis, with a particular focus on propene epoxidation and ketone ammoximation, which are currently two crucial industrial-scale processes that utilise preformed H$_2$O$_2$ with the titanosilicate catalyst TS-1 for chemical synthesis. This contribution will highlight the potential for in-situ H$_2$O$_2$-mediated feedstock upgrading to replace existing technologies and contribute to the declared sustainability goals of the chemical synthesis sector.

Keywords: Selective Oxidation, TS-1, Green Chemistry, In-situ Synthesis, H$_2$O$_2$, Au/Pd-based Catalysts.

1. Introduction

Oxidation reactions employing hydrogen peroxide (H_2O_2), such as ketone ammoximation, olefin epoxidation, aromatic hydroxylation and alkane oxidation, have gained substantial recognition for their environmentally friendly attributes and improved atom- and energy-efficiency compared to alternative approaches [1]. The current industrial-scale production of H_2O_2 is dominated by the well-established anthraquinone oxidation (AO) process, which was first pioneered by Riedl and Pfleiderer of BASF in 1939 and is responsible for over 95% of global H_2O_2 production. This highly efficient process, which relies on the hydrogenation and sequential oxidation of quinone carriers, yields H_2O_2 concentrations exceeding 70 wt.% through successive purification and distillation steps. Beyond chemical synthesis, the industrial applications of H_2O_2 span a wide spectrum, encompassing its utilization as a bleaching agent in the paper and textile industries, water disinfection, and diverse applications such as in metallurgy (Fig. 1a) [2].
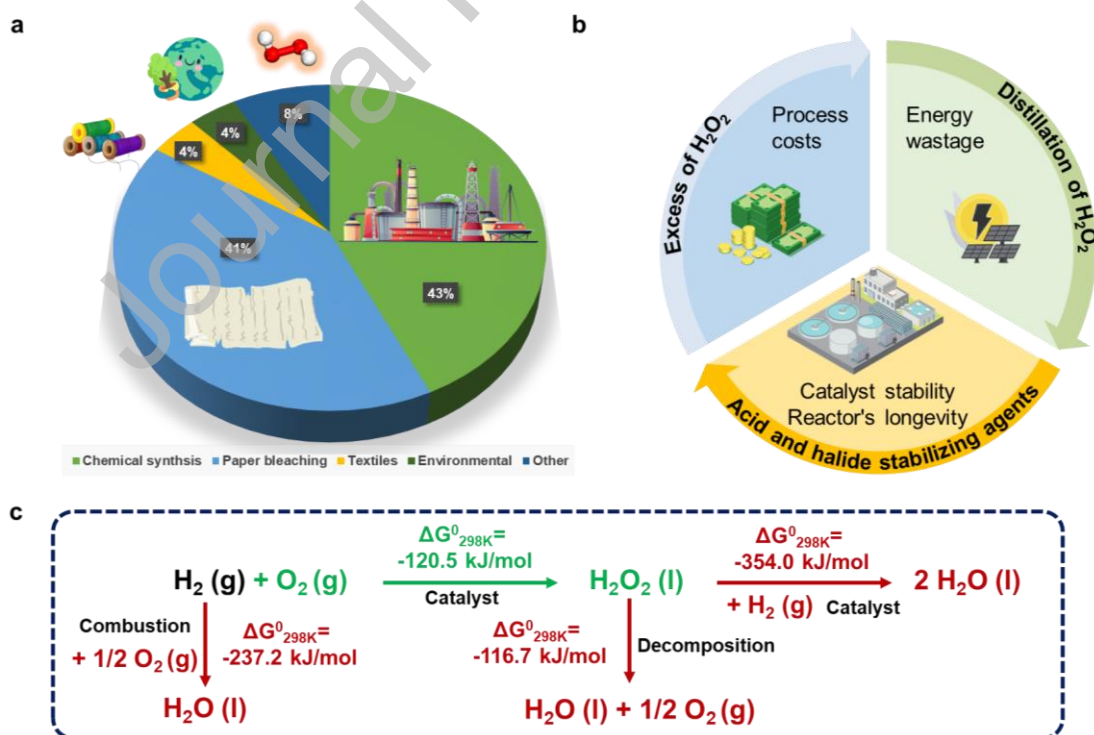

Fig. 1. (a) The application of H_2O_2 by sector. (b) Disadvantages of chemical transformations

reliant on preformed H_2O_2. (c) Reaction pathways associated with the direct synthesis of H_2O_2 from H_2 and O_2.

Within the realm of chemical synthesis, preformed H_2O_2 has found widespread application, with the hydrogen peroxide to propene oxide (HPPO) process and the ammoximation of cyclohexanone to cyclohexanone oxime (a pivotal intermediate in the production of caprolactam and Nylon-6), perhaps the best-known examples of industrial-scale application.

Nevertheless, the inherent low stability of H_2O_2, prone to decomposition even under moderate temperatures or alkali conditions, often mandates the application of an excess of the oxidant, consequently escalating process costs. Moreover, centralized production, driven by economies of scale, results in the distillation of H_2O_2 to concentrations well beyond the needs of end users. The excessive dilution of the oxidant for end users effectively squanders the energy invested in its concentration before transportation. Moreover, the addition of acid and halide stabilizing agents, which is imperative in prolonging the shelf life of H_2O_2, can compromise catalyst stability, reduce reactor longevity (due to corrosion), and incur substantial expenses related to their removal from product streams. These challenges are intrinsic to all chemical transformations reliant on preformed H_2O_2 to varying degrees (Fig. 1b) [2]. The in-situ synthesis of H_2O_2 is steadily gaining prominence as a solution to address these challenges. When H_2O_2 is generated and rapidly utilised in feedstock valorisation, the limitations associated with the use of the preformed oxidant may be effectively mitigated.

The direct synthesis of H_2O_2 from molecular H_2 and O_2 represents an attractive alternative approach to the current commercial route to production. Pd-based catalysts have long been recognized for their pronounced activity in the direct synthesis of H_2O_2, attracting considerable attention in the academic and patent literature [3]. However, a formidable challenge associated with the direct synthesis of H_2O_2 revolves around catalyst selectivity, which can be attributed to the thermodynamic favourability of competitive degradation pathways over H_2O_2 synthesis (Fig. 1c).

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Such selectivity concerns have been addressed through the utilisation of acidic or halide stabilisers or the formation of bimetallic alloys. The introduction of Au into Pd-based catalysts has proven to be highly effective in promoting H_2O_2 selectivity [4]. Significantly, there has been a surge in focus on utilizing alternative secondary metals in recent years, notably non-precious ones like Sn, Ni, and Zn. These catalysts have shown comparable performance to AuPd catalysts [5], with their promotive effects stemming from the formation of bimetallic alloys. This phenomenon is widely attributed to a combination of electronic modification of Pd species and the inhibition of contiguous Pd ensembles, which otherwise tend to engage in competitive degradation pathways.

Although many catalytic materials have been devised to achieve nearly complete selectivity towards H_2O_2 under idealized conditions, coupling ex-situ produced H_2O_2 via the direct process with chemical upgrading would not surmount the numerous challenges associated with H_2O_2 generated via the AO process. Among these challenges, a prominent concern is the typically low concentrations of H_2O_2 achieved by the direct approach. This limitation often arises due to the necessity of using diluted feeds of gaseous reagents to operate safely outside the explosive regime (4-96% H_2). However, such financial and environmental concerns do not exist if H_2O_2 can be generated in-situ and subsequently utilised in oxidative chemistry.

2. Challenging Industrial Technologies with in-situ synthesised H_2O_2

The combination of H_2O_2 with the titanosilicate TS-1 has found widespread application in the oxidative valourisation of several relatively small molecules, as dictated by the limited pore size of TS-1 (~ 5.5 Å), these include alkene epoxidation, aromatic hydroxylation, ketone ammoximation, alkane oxidation, as well as the oxidation of sulfides and alcohols (Fig. 2) [6]. However, it is the epoxidation of propene and the ammoximation of cyclohexanone that represent the most pertinent examples of TS-1/H_2O_2-mediated chemistry.
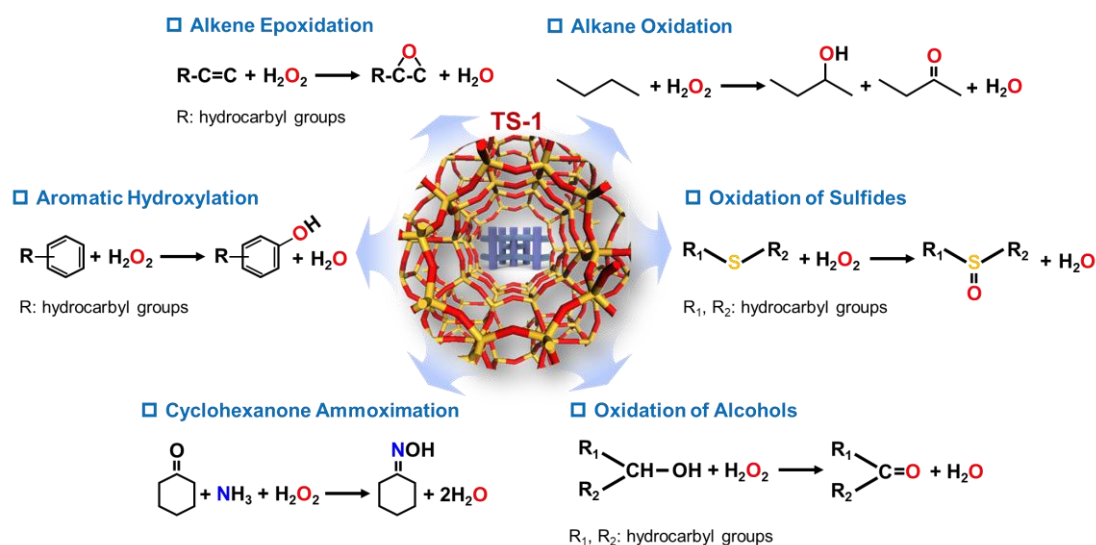
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Fig. 2. The wide-ranging application of TS-1 and H_2O_2 for chemical synthesis.

2.1 Direct propene epoxidation.

The drawbacks of the industrial epoxidation of propene through the two-stage chlorohydrin or organic hydroperoxides technologies have been largely overcome via the implementation of the HPPO process. Notably, Polimeri Europa has patented an integrated plant where hydrogen peroxide is produced in situ via AO method [7]. This process has the advantage of eliminating the necessity of H_2O_2 extraction and successive concentration by distillation, resulting in a considerable reduction in energy utilisation. However, the reported yield of propene oxide was lower than that reported for the ex-situ HPPO processes. A one-step alternative via in-situ H_2O_2 synthesis has been a major area of interest since the first reports by Haruta and co-workers [8] and has the potential to offer improved efficiencies compared to alternative processes. In particular, Au nanoparticles deposited on titanosilicates have been extensively reported to offer high efficacy towards the in-situ epoxidation of propene. A rich body of literature has since developed since the early works of Haruta, with the formation of 3-dimensional mesoporous, significantly improving catalyst efficacy. Further works have described how the transfer of Au complexes into the titanosilicate micropores can be influenced by Au speciation and the pore properties of TS-1 during catalyst synthesis. Through careful selection of these key parameters

can dictate the preferential formation of distinct Au sites within the micropores, consequently resulting in different catalytic performances.

In particular, solid/gas and solid/gas/liquid methodologies, revolving around bifunctional Au/TS-1 catalysts, have garnered considerable interest. In this approach, H_2O_2 synthesized over Au species is then leveraged by Ti sites within the TS-1 to catalyze propene epoxidation, although catalysts based on alternative noble or earth-abundant metals (or a combination thereof) have also been reported. Activating molecular oxygen and hydrogen to generate H_2O_2 over metal sites is mainly regulated through three aspects: electronic properties, size effects, and spatial distribution. Notably in the case of the Au/TS-1 system, the potential for the metallic species to be directly involved in the epoxidation mechanism has also been identified, although the contribution to epoxide formation over Au directly is considered to be relatively minor. Recently the widely accepted H_2O_2 activation mechanism centred around isolated Ti^{4+} sites (Fig. 3a) [10] has also been challenged, with a combination of ^{17}O NMR, electron microscopy and theoretical studies providing robust evidence for the involvement of dinuclear Ti-sites (Fig. 3b) [11]. Moreover, it was found that the epoxidation of propene near a Si vacancy follows a two-step pathway. Initially, H_2O_2 forms a hydroperoxy intermediate (Ti-OOH) over Ti active sites. Subsequently, the intermediate reacts with propene through proximal oxygen abstraction. The abstraction step is significantly facilitated by a simultaneous hydride transfer, involving neighboring terminal silanol groups originating from the Si vacancy [12]. Regardless a major challenge of the in-situ approach is associated with catalyst deactivation, primarily through metal agglomeration or coking. In particular, the deactivation of Au/TS-1 in in-situ propene epoxidation has been attributed to the blocking of micropores by carbonaceous deposits. Notably, the use of uncalcined TS-1 (i.e. with blocked pores), has been shown to be highly stable and also offer reasonable activity towards the epoxidation reaction.

In both gas and liquid phase methodologies, inefficient H_2 utilization emerges as a significant challenge. This inefficiency leads to the decomposition of in-situ

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synthesized H_2O_2 and formation of relatively large quantities of acetone, propanal, ethanal, acrolein, and CO_2. Additionally, catalytic oxidation of solvent systems has been reported, which further complicates any potential liquid phase in-situ approach. Such challenges are considerable and must be overcome if the in-situ approach is to challenge existing technologies. However, recent advances to inhibit (re)adsorption of the epoxide and improve catalytic selectivity and stability are particularly promising [13] and may be key to the future industrialization of in-situ propene epoxidation. Furthermore, improving long-term catalytic stability and hydrogen efficiency, along with developing improved reactor designs concurrent and process optimization, are key factors in accelerating the industrialization of the in-situ approach to propene epoxidation. In addition to propene, it is advisable to take into account other alkenes (e.g., butene, 1-hexene and cyclohexene) when aiming to achieve direct epoxidation using H_2 and O_2. This approach helps in addressing the limitations associated with the conventional process of alkene epoxidation involving preformed H_2O_2.
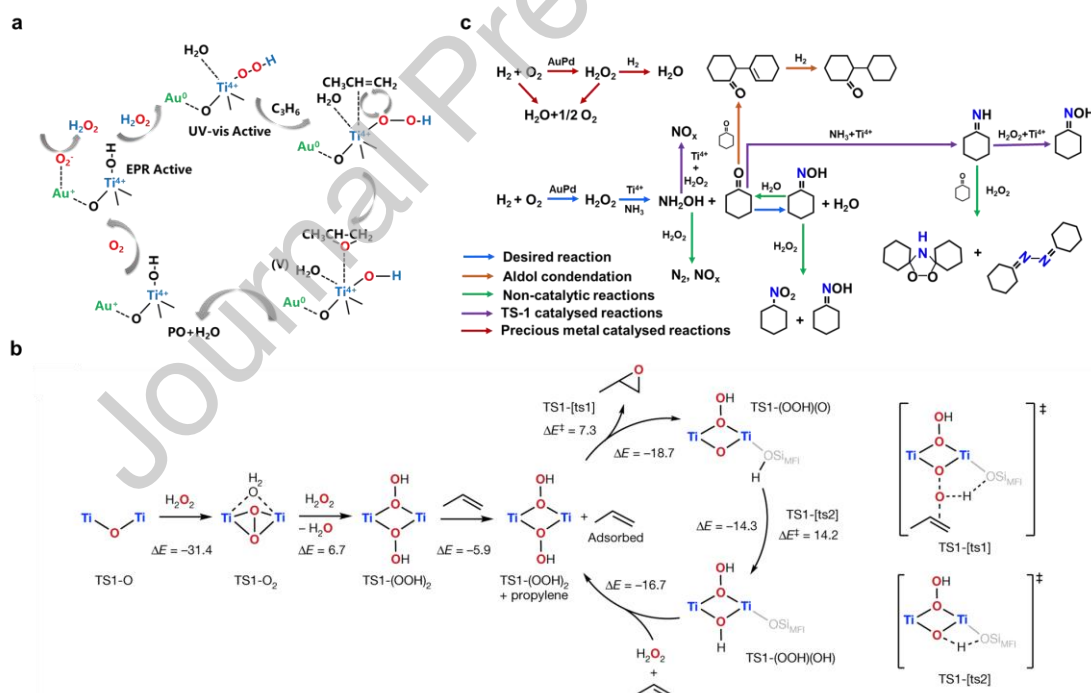

Fig. 3. (a) The proposed 'isolated Ti^{4+} site' mechanism for propene epoxidation via in-situ H_2O_2 synthesis over Au/TS-1. (b) The simulated reaction pathway of propene epoxidation by H_2O_2 on dinuclear Ti sites. (c) The proposed reaction pathway for cyclohexanone ammoximation via in-situ H_2O_2 synthesis, over a AuPd/TS-1 catalyst.

2.2 Cyclohexanone ammoximation.

As with propene epoxidation, the adoption of a TS-1/H_2O_2-mediated approach to ketone (particularly cyclohexanone) ammoximation has offered considerable advances over prior technology and is now considered the state-of-the-art approach to oxime production. Indeed, with extensive process optimisation exceptional selectivities to the oxime have been reported [14, 15]. Until recently, efforts to develop an integrated ammoximation process had been complicated by poor selectivity and the use of complex reaction media. For example, the supply of H_2O_2 via the partial oxidation of isopropanol yields appreciable concentrations of impurities. These challenges have been completely avoided through the development of a series of composite catalysts, such as AuPd/TS-1 [16] and AuPdPt/TS-1 [17]. Similar to the approach employed for propene epoxidation, these catalysts combine the precious metals (Pd-based in this case) for H_2O_2 synthesis with the framework Ti sites. The latter are responsible for synthesizing the hydroxylamine intermediate from H_2O_2 and NH_3, which then undergoes a non-catalytic reaction with the ketone to form the oxime (refer to Fig. 3c). In particular, the performance of the AuPd/TS-1 catalyst has been shown to rival that of the industrial process, under industrially relevant conditions, with oxime yields approaching 90% observed under industrially relevant conditions. Importantly, when ketone conversion is limited (~30%) near-total selectivity based on H_2 may be achieved, with this metric decreasing to approximately 70% when the process is operated at high cyclohexanone conversion rates (> 95%).

This loss in selective H_2 utilisation may be attributed to the use of excess H_2 (in comparison to the ketone) and the ability of the AuPd catalyst to catalyse competitive H_2O_2 degradation (via hydrogenation and decomposition pathways). This lossed H_2 utilisation should not be attributed to the generation of hydrogenated by-products, with oxime selectivities in excess of 95% observed, regardless of substrate (ketone and H_2) conversion rates. Such observations perhaps highlight the need for the use of successive reactor systems, where ketone conversion at each stage is limited or the

adoption of semi-continuous or continuous reactor technology. Importantly, these observations also highlight the need for the careful selection of both catalyst formulation and process parameters.

The presence of alloyed AuPd species has been found to be crucial in achieving high catalytic performance, with Pd-only formulations rapidly deactivating through metal dissolution, while the performance of Au-only analogues are limited by their poor activity towards H_2O_2 formation. Alternative Pd-based catalysts, including PdSn, PdNi, and PdZn, were found to be largely ineffective. This is noteworthy despite the well-documented activity of such formulations towards H_2O_2 synthesis under conditions optimized for H_2O_2 stability. Metal leaching, as observed in Pd-only systems, might account for this ineffectiveness. A detailed techno-economic assessment, which compares the in-situ methodology with the current industrial process utilizing preformed H_2O_2, has been conducted, indicating the potential for a 13% reduction in costs, based solely on material expenditures, assuming a catalyst lifespan of 2.3 years. Notably, even with a more limited catalyst lifespan (0.75 years), the economic analysis suggests that the material costs associated with the in-situ approach are comparable to those of the existing industrial process. Consequently, the adoption of the in-situ pathway signifies a positive step towards a more sustainable and efficient route to cyclohexanone ammoximation, with the potential to surpass the current industrial methodology. However, while such observations are encouraging and may highlight the potential benefits of in-situ H_2O_2 synthesis, it is important to note the need for further evaluation at scale.

3. Conclusion and Future Perspective

The in-situ synthesis of H_2O_2 over bifunctional composite catalysts that are able to both synthesize the oxidant and subsequently utilize it in chemical synthesis represents an attractive alternative to a number of oxidative transformations, with the promise of an integrated approach to ketone ammoximation considered to be particularly exciting. However, it is clear that further evaluation at industrially relevant timescales is still required.

For processes utilizing in-situ synthesized H_2O_2, several challenges persist. It is crucial to achieve near-complete selective utilization of H_2 to ensure high process efficiency and competitiveness compared to that of current technology. This becomes especially critical due to the potential formation of hydrogenation byproducts and the likelihood of active metals catalyzing H_2O_2 degradation. Clearly, there is a need to strike a balance between the rate of H_2O_2 synthesis and the capacity of TS-1 to selectively utilize the oxidant. Therefore, a comprehensive approach to catalyst development, addressing both the active metals and the titanosilicate, is recommended. In light of the promising results obtained with the in-situ H_2O_2/TS-1 approach, there is evident potential to explore alternative titanosilicates that are not constrained by the small pore size of TS-1, enabling the selective oxidation of a broader range of chemical substrates.

Declaration of competing interest

The authors declare that they have no conflicts of interest in this work.

Acknowledgments

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Declaration of Interests

☒ 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 authors declare the following financial interests/personal relationships which

may be considered as potential competing interests: