

Review

Theoretical Studies on the Direct Propylene Epoxidation Using Gold-Based Catalysts: A Mini-Review

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Abstract: Direct propylene epoxidation using Au-based catalysts is an important gas-phase reaction and is clearly a promising route for the future industrial production of propylene oxide (PO). For instance, gold nanoparticles or clusters that consist of a small number of atoms demonstrate unique and even unexpected properties, since the high ratio of surface to bulk atoms can provide new reaction pathways with lower activation barriers. Support materials can have a remarkable effect on Au nanoparticles or clusters due to charge transfer. Moreover, Au (or Au-based alloy, such as Au-Pd) can be loaded on supports to form active interfacial sites (or multiple interfaces). Model studies are needed to help probe the underlying mechanistic aspects and identify key factors controlling the activity and selectivity. The current theoretical/computational progress on this system is reviewed with respect to the molecular- and catalyst-level aspects (e.g., first-principles calculations and kinetic modeling) of propylene epoxidation over Au-based catalysts. This includes an analysis of H₂ and O₂ adsorption, H₂O₂ (OOH) species formation, epoxidation of propylene into PO, as well as possible byproduct formation. These studies have provided a better understanding of the nature of the active centers and the dominant reaction mechanisms, and thus, could potentially be used to design novel catalysts with improved efficiency.

Keywords: propylene epoxidation; gold; computational chemistry; active centers; reaction mechanisms

1. Introduction

Due to the growing environmental issues in chemical synthesis and processing, there has been increasing interest in the development of new processes for minimizing pollution and reducing energy consumption. Heterogeneous catalysis plays a crucial role in this respect, since it is widely used to reduce emissions from automobiles, reduce byproducts, and improve the selectivity of important chemical products in the petrochemical as well as other chemical industries [1–5]. Computational and experimental investigators have been working together to better understand fundamental characteristics of a wide range of catalytic reactions. In this paper, we focus on the selective epoxidation of propylene to yield propylene oxide (PO) using heterogeneous gold-based catalysts. The catalytic activity of gold and gold alloy nanoparticles (a few nm in size) has been ascribed to various mechanisms, involving reactions occurring at neutral gold atoms that differ from bulk gold atoms (due to different degrees of coordination), quantum size effects that change the electronic structures of nanoparticles, or charge modification of gold atoms through the interaction with oxide supports [6–8].

Computational studies have been enormously valuable in describing the structural and electronic character of size-selected gold nanoparticles and determining the catalytic reaction mechanisms for the propylene epoxidation process, and have already yielded important outcomes for the development of catalytic materials. Motivated by these growing computational investigations and the need to incorporate this theoretical knowledge into catalyst design, we review the theoretical studies relevant to direct propylene epoxidation in the gas phase with Au-based catalysts. In the following sections, we provide a brief background of propylene epoxidation, and we then highlight different aspects of the propylene epoxidation process, including H_2/O_2 adsorption, H_2O_2 synthesis, and possible epoxidation mechanisms. Finally, conclusions and perspectives are given, along with current challenges and opportunities in the field.

2. Background

Propylene oxide (PO) is a key intermediate in the chemical industry. For instance, PO is mainly used to produce polyether polyols (65%), as well as propene glycol (30%) and propene glycol ethers (4%) (the second and third largest applications, respectively), which are mainly applied to manufacture commercial products such as adhesives, solvents, and foams [9–11]. The annual worldwide production of PO in 2013 amounted to 8.06 million tons and will likely go beyond 9.56 million tons in 2018, and this market is annually growing by ~4–5% [11]. The currently available processes are not optimal, since the chlorohydrin process to produce PO suffers from environmental concerns, and the hydroperoxide process (the halcon process) is challenged by poor economics [9,11]. For instance, in the chlorohydrin process, a large amount of byproduct $CaCl_2$ (2.2 tons per 1.0 ton of PO) is coproduced, along with toxic chlorinated organic compounds (several hundred grams per ton of PO). One problem of the hydroperoxide process is the production of a coproduct (either styrene or *tert*-butyl alcohol, depending on which variant of the hydroperoxide process is applied) in a fixed amount, leading to a mismatch of market demand between PO and co-products.

Compared to the two methods aforementioned, using hydrogen peroxide (H_2O_2) as the oxidant allows for a high selectivity (95%) for PO production, and it is more environmentally friendly since water is the only byproduct. The major disadvantage for the commercialization of this process is that hydrogen peroxide and PO have comparable market values on a molar basis, which makes it impossible to run the process profitably at this time. Moreover, it requires multiple reaction steps in the liquid phase for purification, which consumes huge amounts of energy. The *in situ* production of the hydrogen peroxide is currently under construction by Dow-BASF, to solve the high cost of hydrogen peroxide for propylene epoxidation [12].

Another route toward PO production is the direct propylene (C_3H_6) epoxidation using gold/titania catalyst in the presence of a mixture of hydrogen and oxygen. For a long time, coinage metal gold was regarded as a catalytically inert material. This common assumption was dramatically shifted by the discovery of low-temperature CO oxidation with metal oxide supported gold nanoparticles [13]. Approximately 20 years ago, Haruta and co-workers discovered that the direct vapor-phase propylene epoxidation with molecular H_2 and O_2 catalyzed by nano-sized gold deposited on TiO_2 (anatase) was a viable route [14]. The largest advantage of gold-on-titania catalysts is that they are able to epoxidize propylene very selectively (>90%) even under mild conditions (typically 323 K and 1 bar), but the activity is relatively low.

Since that time, considerable efforts have been dedicated to enhancing Au-based catalysts, as well as understanding the reaction features of this novel system. For instance, gold particles which are hemispherical in shape are highly active, while spherical nanoparticles possess fairly weak activity [15]. Estimates of the optimal gold nanoparticle size have reduced from 2–5 nm in diameter to sizes smaller than 2 nm [11,14,16–18]. Haruta's group initially started working with Au nanoparticles supported on TiO_2 , but they gradually transitioned to mesoporous titanasilicates ($Ti-SiO_2$) as the supports [19,20]. Delgass's group has focused on microporous titanasilicate (e.g., TS-1) supports, which demonstrate better results, even with low Au loadings [21,22]. The fact that the PO formation requires the presence

of H_2 and O_2 , and the fact that C_3H_6 can be epoxidized by H_2O_2 over titania, generates the common speculation that a peroxide species formed on gold is involved in the propylene epoxidation reaction. In other words, it is proposed that the active oxygen species, hydrogen peroxide, is readily synthesized on nano-sized Au via H_2/O_2 mixtures, and it subsequently transfers to a neighboring Ti site to epoxidize propylene into PO. During this process, the typically low propylene conversion (<2%) and low hydrogen utilization efficiency (<30%) still need to be improved, despite the fact that the selectivity toward PO is high.

Attempts to improve propylene conversion by raising the reaction temperature inevitably lead to decreasing PO selectivity due to consecutive PO reactions (e.g., isomerization, oligomerization, and oxidative cracking) [17,23–26]. For instance, by elevating the reaction temperature from 90 °C to 160 °C, there is an appreciable increase in C_3H_6 conversion from 2.5 to 9.8% over Au/mesoporous Ti-SiO₂, while the PO selectivity decreases from 95 to 90%. The decrease in selectivity is likely due to the formation of byproducts (e.g., propanal, acetone, ethanal, CO₂, dioxane, and acids) generated by secondary reactions [19,27]. The byproduct generation is proposed to be related to the dispersity of Ti sites. For example, PO combustion is significantly suppressed if Ti sites are isolated, as in TS-1 and in mesoporous Ti-SiO₂ [28,29]. It is worth noting that acrolein is another significant byproduct [25]. The allylic hydrogen of propylene is acidic and labile, and easily suffers from the nucleophilic attack of the oxygen radicals bound to Au nanoparticles, since the oxygen species behave as a Brønsted base [10,30–32]. Thus, silver-based catalysts, used for commercial production of ethylene oxide (EO) via ethylene epoxidation, lead to propylene combustion versus epoxidation due to the activation of allylic hydrogen by surface O. On the other hand, investigations with regard to gold catalysts indicate that they may be commercially feasible for propylene oxide production [33].

To date, there have been several reviews about the experimental synthesis of PO in the gas phase, including discussions about the development and improvement of Au-based catalysts, propylene conversion, hydrogen efficiency, and PO selectivity [9,11,16,17,34]. At the same time, many theoretical studies have focused on propylene epoxidation with H_2 and O_2 to assist in understanding various aspects of this catalytic reaction. For instance, first-principles calculations can be employed to investigate the elementary events and underlying mechanisms, but it is usually difficult to make statements about the performance of the catalysts under different reaction conditions. In this respect, kinetic modeling studies are needed to evaluate the catalytic activity and product selectivity at larger time and length scales, particularly with several competing reaction pathways. For instance, first-principles based kinetic Monte Carlo (KMC) models can help unravel the reaction mechanism and catalyst complexities in heterogeneous catalytic systems [35–38]. These computation and simulation studies provide detailed insight on how to screen the size and composition of Au nanoparticles, as well as identify catalytic sites and reaction features for the development of commercially viable catalyst for direct PO production.

3. The Adsorption of O_2 and H_2 on Au

Bulk gold surfaces are usually regarded as poor catalysts, at variance with other transition metal surfaces. However, as compared to Au surfaces, small Au particles are known to be active catalysts for a variety of reactions. The adsorption of molecular O_2 and H_2 on small Au clusters in the gas phase is the first step of the overall propylene epoxidation reaction. Thus, this is a key step, since the adsorption energy (E_{ads}) can be used as an indicator of activity, and it is helpful for developing a comprehensive understanding of Au catalysis.

Salisbury and co-workers investigated O_2 adsorption on Au_n^- clusters ($n = 2$ to 22). They found that Au_n^- clusters with even n strongly adsorb O_2 molecules, while Au_n^- clusters with odd n cannot. Salisbury et al. supposed that the adsorbed oxygen molecule exists in the form of O_2^- species due to charge transfer from the gold [39].

Okumura et al. and Yoon et al., using density functional theory (DFT), studied the interaction between O_2 and Au clusters [40,41]. They found that the anionic Au atoms in gold clusters interact

strongly with O₂ (−12.1 kcal/mol), in contrast with neutral Au atoms (−3~8 kcal/mol), suggesting that negatively charged Au atoms are the active sites for oxygenation. As an extension, Mills et al. suggested that neutral Au_{*n*} clusters with an odd *n* adsorb O₂ more strongly in contrast with those with even *n* [42], which agrees well with the recent findings of Chen's group [43]. At the same time, they mentioned that O₂ does not adsorb on flat Au surfaces, indicating that the interaction between O₂ and an Au surface is weak. While in the DFT studies of Mavrikakis and coworkers, they found that, although molecular O₂ does not adsorb on Au(111), it does bind to a stretched Au(111) surface, as well as to both unstretched and stretched Au(211) surfaces with binding energies of −1.84, −3.46, and −6.0 kcal/mol, respectively, implying that steps and tensile strain facilitate the adsorption of O₂ on Au surfaces [7,44].

There is a general agreement regarding the relationship between the increasing activity of gold nanoparticles and a decrease in particle size (leading to a higher concentration of low coordinated gold atoms), as well as particle morphology [6,45]. For instance, Wang and Gong found that an icosahedral Au₃₂ cluster can dissociate molecular O₂, but the detailed dissociation pathways and the activation energies are not described [46]. Taketsugu et al. studied O₂ adsorption on small neutral gold clusters (Au₃–Au₁₂), and found that O₂ adsorption induced structural transformations in gold clusters [47]. Pacchioni et al. also studied O₂ adsorption and dissociation on neutral, positively, and negatively charged Au_{*n*} clusters varying from 5 to 79 atoms [48,49]. It was found that the charging effect of gold clusters is prominent for very small sizes up to about 20–25 gold atoms, in which negatively charged gold clusters are beneficial for O₂ activation, while positively charged clusters are not. The effect of charge disappears with the increasing gold cluster size, and Au₃₈ seems to be the most reactive. When the cluster size increases beyond about 40 atoms, the effect of size and shape becomes a more significant factor governing the reactivity. The electronic properties beyond Au₇₉ linearly scale to the bulk gold properties, and the catalytic activity thus gradually dies out [50].

Corma's group, using DFT calculations, investigated the adsorption and dissociation of O₂ on extended Au(111) and Au(100) surfaces, isolated Au nanoparticles with different sizes (Au₁₃ and Au₃₈) and shapes, and Au nanoparticles supported on TiO₂ [51]. The adsorption energy of O₂ was found to be correlated with gold particle size, and the particle morphology was proved to be a crucial factor for activating O₂ dissociation. They found a linear relationship between the activation energy of O₂ and the net charge on adsorbed O₂, indicating that the degree of charge transfer determines the molecular O₂ activation. Moreover, they discovered that most of the sites for O₂ adsorption and dissociation are located at the Au/support interface (when gold particles are loaded on a TiO₂ support). This is in good agreement with other investigations, with regard to the high catalytic activity of gold particles loaded on metal oxide supports such as CeO₂, TiO₂, and Fe₂O₃ [6,52–57], as well as metal carbides [58]. Nevertheless, there is still a debate about whether the supports are involved in the formation of charged (positively or negatively, depending on oxidized or reduced support surfaces) Au sites due to a transfer of electron density, if they are involved in the activation of reactants (e.g., O₂), or if they are limited to merely stabilizing the gold particles [59–61].

The adsorption of O₂ on alloy clusters of gold has also been investigated [62,63]. Joshi et al. analyzed the adsorption of O₂ on Au_{*n*}M_{*m*} (*m, n* = 0 to 3; M = Cu, Ag, Pd, Pt, and Na) clusters, in which they demonstrated that the alloy trimers containing only one Au atom are most reactive toward O₂, while those with two Au atoms are least reactive [63]. The O₂ binding energy (BE) follows the trend: BE (MAu₂) < BE (M₃) ≤ BE (M₂Au). A Natural Bond Orbital (NBO) analysis indicated that all of the clusters donate electron density to the adsorbed O₂. Polynskaya et al. calculated the adsorption energies of O₂ on clusters (following the order: Au₂₀ < Au₁₉Ag < Ag₁₉Au ≈ Ag₂₀), and they found dissociative O₂ adsorption is possible on Au₁₉Ag, Ag₁₉Au, and Ag₂₀ clusters [64]. Recently, Feng et al. compared the adsorption of O₂ on the surfaces of pure Au nanoparticles and Au–Ag bimetallic nanoparticles, and found that O₂ adsorption on the Au–Ag alloy is stronger [65]. Their Bader charge calculations showed that the Au atoms on the surface of Au–Ag alloy nanoparticles are negatively charged (prior to O₂ adsorption), implying that there is electron transfer from Ag to Au. When O₂

adsorbs on the pure Au or Au–Ag alloy nanoparticles, the adsorbed O₂ can accept electron charge from both nanoparticles, but the O₂ withdraws more charge from the Au–Ag nanoparticle surface than from the pure Au nanoparticle surface. This suggests that the bimetallic Au–Ag nanoparticles tend to donate more electrons to the adsorbed O₂, thereby facilitating O₂ activation.

In contrast with relatively weak O₂ adsorption on Au, H₂ adsorption on Au usually follows a dissociative pathway. Gordon's group investigated the reactions of molecular hydrogen with small gold clusters and showed that molecular H₂ easily binds to neutral Au₂ and Au₃ clusters, and then dissociates into two hydrogen atoms [66]. Through DFT calculations, Barrio et al. studied the interaction between H₂ and Au(111), Au(100), and Au clusters (Au₁₄, Au₂₅, and Au₂₉). They found that the H–H bond was spontaneously elongated up to cleavage, without an apparent activation barrier, when H₂ approached the Au clusters. H₂ dissociation was also found to be accompanied by the deformation of clusters in order to stabilize the dissociated H atoms. This is different from H₂ dissociation on the more rigid icosahedral Au₁₃ cluster, with an activation energy of 6.93 kcal/mol [67]. Recently, studies of H₂ adsorption and dissociation on gold clusters demonstrated not only that the effect of low coordinated Au atoms is important, but also that the fluxionality (the flexibility of the structure) and ensemble effects play key roles in the bonding and dissociation of H₂ [68]. Simultaneously, Barrio et al. found that the flat (111) and (100) surfaces of bulk gold are not active towards H₂ dissociation [69,70], which is in agreement with previous studies [71]. Flores et al. also obtained a similar conclusion that stretched gold nanowires are more catalytically active for H₂ dissociation in comparison to the Au(111) surface (H₂ dissociation barriers: 9.22 vs. 23.06 kcal/mol) [72].

In addition to Au surfaces and nanoparticles, H₂ dissociation at the perimeter sites of Au/TiO₂ has been explored by several groups. For instance, Hu et al. investigated the dissociation of molecular H₂ at an Au/TiO₂ interface, as well as atomic H spillover from Au nanoparticles to a TiO₂ support [73]. In their studies, H₂ dissociation is possible via two different modes, namely homolytic and heterolytic routes. In the homolytic pathway, H₂ dissociates on the Au atoms only, while in the heterolytic one, H₂ dissociation occurs on one Au atom and a nearby surface O (from TiO₂). It was found that the heterolytic dissociation of molecular H₂ is more favored than the homolytic dissociation (with activation barriers of 8.53 vs. 14.76 kcal/mol) at the perimeter sites of Au/TiO₂. Using DFT calculations, Takeda's group verified the transition state structure O^{2−}–H⁺–H–Au of H₂ dissociation at the perimeter of TiO₂, as Hückel's theory initially suggested [74]. Simultaneously, they demonstrated that H₂ dissociation at the perimeter sites has the lowest activation barrier (6.23 kcal/mol) in contrast with those on Au(100), Au(321), and the TiO₂ support (17.53, 14.76, and 18.68 kcal/mol, respectively). The calculated activation barrier of 6.23 kcal/mol is consistent with the theoretical result (6.69 kcal/mol) from Hu's group aforementioned but is higher than the reported 3.69 kcal/mol from Neurock's group [75]. Their results are lower than the experimental estimate of 8.76 kcal/mol [76].

4. The Synthesis of H₂O₂ from O₂ and H₂

Hydrogen peroxide (H₂O₂) is a green oxidant, and it has been listed as one of the 100 most important chemicals in the world [77]. The annual worldwide production of H₂O₂ in 2010 was about 3 million tons [78], in which the auto-oxidation (AO) method accounts for more than 95% of the synthesis. However, the AO process is accompanied by problems of exhaust gas emission, solid waste, and waste water [77]. Currently, most commercial H₂O₂ production is directed towards applications in wastewater treatment, hydroquinone production, bleaching of textile and pulp, removal of organic pollutants, etc. [79–81]. In recent years, commercial H₂O₂ has been used in chemical synthesis, such as the epoxidation of alkenes [82]. Unlike the AO process, the direct synthesis of H₂O₂ with H₂ and O₂ emerges as an atomically economic and green chemical reaction, catalyzed by noble metals, such as Pd, Pt, Au, and Ru. Since this review focuses on propylene epoxidation with Au-based catalysts, we highlight the relevant theoretical studies of H₂O₂ production from H₂ and O₂ involving gold catalysts.

Thomson's group proposed a reaction path for H_2O_2 formation on a neutral Au_3 cluster as shown in Figure 1 [83]. The first step is nondissociative O_2 adsorption on an Au trimer with an end-on geometry (8.6 kcal/mol binding energy). As molecular H_2 approaches the adsorbed O_2 , the H–H bond gradually elongates to breakage and one H directly bonds to one Au atom, and the other H bonds to an adsorbed O in the form of an OOH intermediate A in Figure 1. The second H_2 then inserts between the nearest Au atom and the oxygen end of the hydroperoxy group (OOH), leading to H_2O_2 formation (Intermediate B in Figure 1). The generated H_2O_2 desorbs, followed by the exothermic addition of molecular O_2 to form Intermediate D, which undergoes a structural rearrangement to regenerate O_2 to form Intermediate A, allowing this catalytic cycle to repeat. The H_2O_2 desorption has the highest activation barrier ($\Delta E^\ddagger = 8.6$ kcal/mol) during the formation of hydrogen peroxide. Likewise, Kacprzak et al. have demonstrated that small neutral gold clusters (e.g., Au_2 and Au_3) can catalyze H_2O_2 formation and have identified possible reaction pathways for both H_2O_2 and H_2O synthesis [84]. MD simulations highlight important fluctuations of the Au cluster during the reaction process, which is consistent with the geometric fluxionality of Au particles aforementioned [60]. Later, Thomson et al. compared the catalytic activity of Au_3 , Au_4 , Au_5 , and Au_7 clusters in the gas phase reaction of H_2 and O_2 to form H_2O_2 [85]. It was found that both neutral and charged Au clusters are active in the peroxide formation reaction, but Au_3^+ is the most active one for H_2O_2 formation based on the Gibbs free energy of activation.

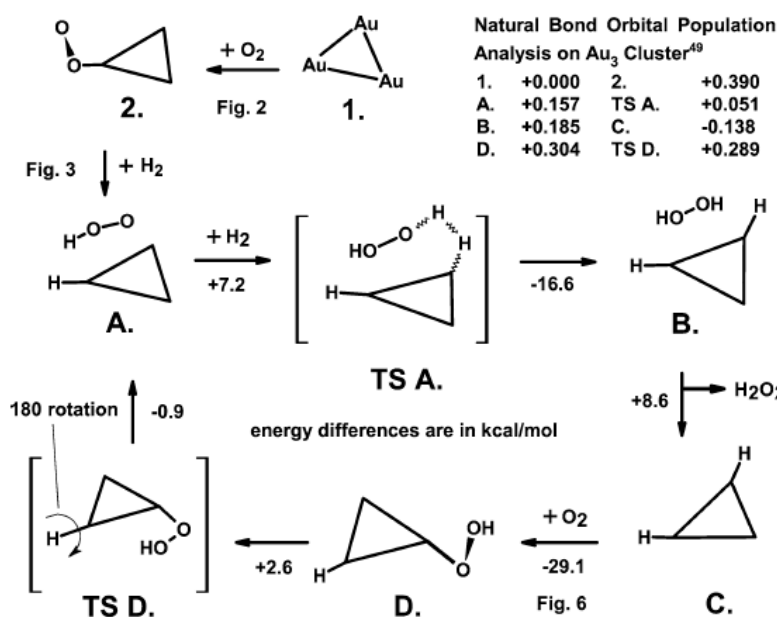


Figure 1. Catalytic cycle for the formation of H_2O_2 over Au_3 (Au_3 cluster is represented by the triangle in each intermediate geometry) with two transition state geometries (TS A and TS B), identified in each intermediate geometry) with two transition state geometries (TS A and TS D), identified with square brackets, and intermediates (A–D). Energy differences are shown in kcal/mol under each reaction arrow [83]. Copyright © 2004 Elsevier Inc.

As mentioned above, the adsorption of O_2 on Au particles is weak. However, it has been shown that the reactivity of $\text{Au}(111)$ and $\text{Au}(100)$ surfaces and clusters toward O_2 is noticeably enhanced with the presence of preadsorbed hydrogen. In this case, the interaction between Au and O_2 becomes stronger due to the formation of O–H bonds, leading to easier formation of the active oxidant species OOH [70]. The hydrogenation of OOH was found to be highly exothermic, with a low activation barrier, thereby allowing the easy and fast formation of H_2O_2 . Moreover, the partial and complete reduction of O_2 by hydrogen on the (111) surfaces of transition metals (e.g., Rh, Ir, Ni, Pd, Pt, Cu, Ag, and Au) have also been systematically studied, and the relevant elementary reactions are listed in Equations (1)–(14) [86]. Several hydrogenated forms of oxygen are investigated as possible reaction intermediates, including peroxy (OOH), aquoxy (OOHH), hydrogen peroxide (HOOH), trihydrogen peroxide (HOOHH), hydroxyl (OH), and water (H_2O). It is clearly seen that the elementary reactions concerning O–O bond breakage (e.g., $\text{O}-\text{O}$, $\text{O}-\text{OH}$, $\text{HO}-\text{OH}$, and $\text{O}-\text{OHH}$) directly or indirectly bring about H_2O formation. The results demonstrate that (1) the dissociative adsorption of O_2 prevails on Rh, Ir, Ni, and Cu facets, and the reduction of the dissociated O species is kinetically hindered due to the strong O binding to the metals; (2) the complete reduction to H_2O

peroxide (HOOHH), hydroxyl (OH), and water (H₂O). It is clearly seen that the elementary reactions concerning O–O bond breakage (e.g., O–O, O–OH, HO–OH, and O–OHH) directly or indirectly bring about H₂O formation. The results demonstrate that (1) the dissociative adsorption of O₂ prevails on Rh, Ir, Ni, and Cu facets, and the reduction of the dissociated O species is kinetically hindered due to the strong O binding to the metals; (2) the complete reduction to H₂O via species OOH, HOOH, and OOHH prevails on Pd, Pt, and Ag, since they are capable of catalyzing O–O bond cleavage and O–H bond formation; (3) Au cannot easily break the O–O bond due to the weak binding of O₂. Therefore, Au is more selective towards the partial reduction of O₂ to generate H₂O₂.

Adsorption



Hydrogenation



O–O bond scission



Desorption



Since Hutchings and coworkers discovered the synergistic effect of bimetallic PdAu on the direct synthesis H₂O₂ in 2002 [87], several analyses of H₂O₂ formation from H₂ and O₂ on alloy clusters have been reported. Through first principles calculations, Thomson's group predicted the catalytic activity of Ag–Au, Cu–Au, and Pd–Au dimers and trimers for H₂O₂ formation, including several elementary steps: (1) molecular adsorption of O₂, (2) the formation of OOH species due to the first H addition, and (3) the formation of H₂O₂ based on the second H addition [88]. For each step, the activation energy (ΔE_{act}) and the change in the Gibbs free energy (ΔG_{act}) were computed. It was shown that the H₂O₂ formation on small Ag–Au and Cu–Au clusters is not feasible, mainly because of the unfavorable thermodynamics of H₂ addition. On the other hand, the formation of the OOH and H₂O₂ species is both thermodynamically and kinetically favorable on the PdAu dimer, while it is thermodynamically unfavorable on PdAu₂ and Pd₂Au trimers. Consequently, the PdAu dimer is proposed as a potentially active cluster for both OOH and H₂O₂ formation (in contrast with other clusters), implying that H₂O₂ formation is very sensitive to the size as well as the composition of the alloying clusters. This result is consistent with Ham's studies [89,90], in which they demonstrated that the surface reactivity of bimetallic alloys is mostly influenced by the creation of unique mixed-metal surface sites (the so-called ensemble (geometry) effect [91]). Three different Pd monomer systems in the slab and cluster geometries involving AuPd_M/Pd(111), AuPd_M/Au(111)

(M represents a Pd monomer), and $\text{Au}_{41}\text{Pd}@Pd_{13}$ are used to examine how surface electronic structure impacts the ensemble effect for H_2O_2 formation. In contrast with $\text{Au}_{41}\text{Pd}@Pd_{13}$ and $\text{AuPd}_M/\text{Au}(111)$ cases, $\text{AuPd}_M/\text{Pd}(111)$ has a higher H_2O_2 selectivity. The $\text{AuPd}_M/\text{Pd}(111)$ shows lower activation barriers for OOH and H_2O_2 formation (12.22 and 8.53 kcal/mol, respectively) compared to that on $\text{Au}_{41}\text{Pd}@Pd_{13}$ (16.60 and 14.30 kcal/mol, respectively) and $\text{AuPd}_M/\text{Au}(111)$ (11.76 and 16.37 kcal/mol, respectively). However, the activation barriers for OOH and H_2O_2 decomposition are higher (18.68 and 7.15 kcal/mol, respectively), as compared to that on $\text{Au}_{41}\text{Pd}@Pd_{13}$ (10.38 and 3.92 kcal/mol, respectively) and $\text{AuPd}_M/\text{Au}(111)$ (7.38 and 5.30 kcal/mol, respectively). The reactivity enhancement of the Pd and Au surface atoms is a consequence of the reduced coordination number, as well as the inherent mechanical strain. As a result, the enhanced activity of Pd and its adjacent Au atoms makes the bond breakage of O–O, O–OH, and HO–OH easier, leading to decreased H_2O_2 selectivity. In the formation of H_2O_2 on Au_{20} and Au_{19}Pd clusters, Beletskaya et al. also concluded that the substitution of gold atoms by palladium in Au_{20} results in an increase in the activity of catalyst for H_2O_2 formation, while low coordinated palladium atoms are also responsible for decreasing the selectivity due to water formation [92].

Yoshizawa et al. examined the formation of H_2O_2 from H_2 and O_2 on Pd(111) and $\text{Au}@Pd(111)$ and 10 possible elementary steps were considered [93–95]. All of the side reactions are involved in O–O bond cleavage (e.g., O–O, O–OH, and HO–OH), leading to the nonselective formation of H_2O . It is proposed that the competition of H_2O_2 and H_2O formation is actually the competition between the O–O bond and O–M bond (M is Pd in the case of the Pd(111) and Au in the case of the $\text{Au}@Pd(111)$). The O–Pd bond is usually stronger than the O–O bonds in the OOH and H_2O_2 species, making the O–O bond breakage facile, while the O–Au bond is generally weaker than the O–O bonds, suppressing the O–O bond dissociation and thus facilitating the release of H_2O_2 . Similar conclusions are also obtained in Todorovic's findings [96], in which they demonstrate that the H_2O formation mainly originates from O_2 dissociation on Pd(111), while it is formed from H_2O_2 decomposition on Au(111). One intuitive explanation is that each additional H atom weakens the bond of the molecular backbone and increases the O–O bond length. Nørskov et al. have shown that the O–O bond length increases as O_2 (1.34 Å), OOH (1.44 Å), and H_2O_2 (1.50 Å) on an Au_{12} cluster [97]. Moreover, using well-established scaling and Brønsted-Evans-Polanyi (BEP) relations in combination with the concept of the degree of catalyst control, they predict a search direction for promising H_2O_2 synthesis catalysts, where binary Au–Pd and Au–Ag alloys are most promising (taking stability considerations into account).

5. PO Reaction Mechanism

Haruta and co-workers first demonstrated the direct propylene epoxidation using gas-phase H_2 and O_2 over Au/ TiO_2 with high selectivity [14]. Since then, Au nanoparticles supported on several other Ti-containing supports (such as TS-1 [10,29], Ti-MCM-41 [98], and Ti-MCM-48 [26]) have been found to be active for propylene epoxidation in the gas phase. In particular, Au nanoparticles loaded on a TS-1 support were first synthesized at Enichem (Italy) [99] and were identified as a possible candidate for the future commercial production of PO. Because of the adequate activity, high selectivity, and extraordinary stability of TS-1, liquid-phase epoxidation using H_2O_2 over TS-1 is feasible for PO production [100,101]. However, in view of the fact that H_2O_2 and PO have comparable market values on a molar basis, currently, it is difficult to run this process profitably. An inelastic neutron scattering (INS) study [102] and in situ UV spectroscopy study [103] have offered direct spectroscopic evidence for the formation of H_2O_2 and the hydroperoxy radical (OOH) species, originating from H_2 – O_2 related reactions over Au/ TiO_2 . Thus, a similar propylene epoxidation mechanism in the gas phase using in situ formed H_2O_2 over Au/TS-1 catalyst is expected.

In many cases, current theoretical studies are on par with classical experimental analyses, so theory and experiment can drive each other towards a better understanding of the catalytic reaction mechanism of propylene epoxidation and catalyst design. In the following sections, we summarize the application of computational catalysis and kinetic modeling for the propylene epoxidation mechanism

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(as well as possible side reactions), involving (1) epoxidation using H_2O_2 over TS-1; (2) H_2O_2 formation
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and propylene epoxidation on Au; and (3) the synergistic effect of an Au/Ti-containing support.

5.1. Reaction Mechanism on Titanosilicate

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In comparison to Au/TiO₂ gold particles supported on titanosilicate (TS-1) present much higher catalytic activity for the direct propylene epoxidation reaction, suggesting that the microstructure of the Ti sites is crucial. Through DFT calculations, Thomson's group demonstrated that the defects (Ti sites located near Si vacancies or Ti substituted on Ti with HfO₂ [32]) in the defects of TS-1 catalysts promote the reactivity of propylene epoxidation with H_2O_2 [52]. The results showed that, in the defect-free model, H₂O₂ formation is endothermic (about 6 kcal/mol) after the addition of H_2O_2 to the hydroxyl group on Ti, and the interaction between propylene and hydroperoxy is highly repulsive. In the defect model, the OOH formation is exothermic (about 9 kcal/mol), and the activation barrier for propylene epoxidation is about 9.5 kcal/mol as propylene approaches the intermediate H₂O₂ (the transition state is exhibited in Figure 3), which is highly exothermic (−41.1 kcal/mol). With regard to the effect of the Ti defect site, they proposed that the absence of one Si atom reduces steric repulsions and the generated defect Ti site is more flexible, thereby stabilizing the transition-state formation through structural relaxation.

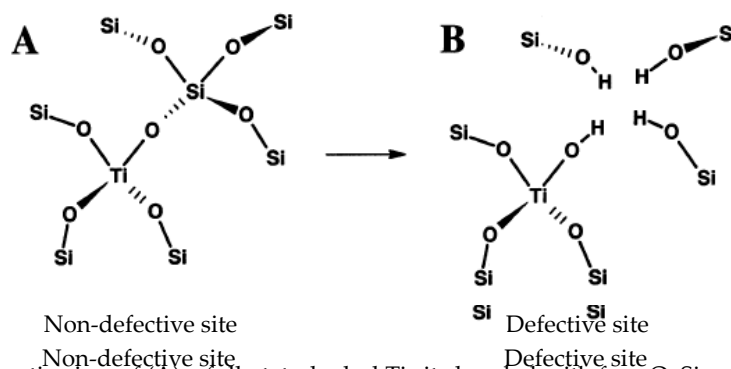


Figure 2. Schematic view of (A) a fully tetrahedral Ti site bonded with four O-Si groups, and (B) the same Ti site located near a silicon vacancy forming a silanol nest [32]. Copyright © 2004 American Chemical Society.

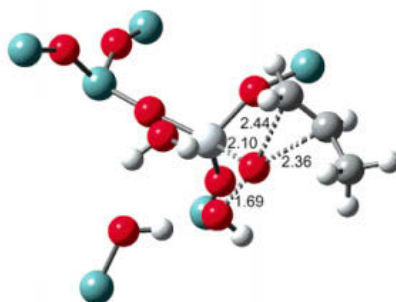


Figure 3. Transition state for the reaction of the hydroperoxy intermediate on a defect Ti site with propylene [32]. Copyright © 2004 American Chemical Society.

Figure 3. Transition state for the reaction of the hydroperoxy intermediate on a defect Ti site with propylene [32]. Copyright © 2004 American Chemical Society.
In their article, Thomson et al. compared five possible mechanisms for propylene epoxidation using H_2O_2 over TS-1 at the same level of theory [164]. The first one is the S_N2-like concerted mechanism, in which the H_2O_2 and propylene approach the Ti site simultaneously. The second one is the S_N1-like stepwise mechanism, in which the H_2O_2 first approaches the Ti site, followed by the propylene. The third one is the S_N2-like concerted mechanism, in which the H_2O_2 first approaches the Ti site, followed by the propylene. The fourth one is the S_N1-like stepwise mechanism, in which the H_2O_2 first approaches the Ti site, followed by the propylene. The fifth one is the S_N2-like concerted mechanism, in which the H_2O_2 first approaches the Ti site, followed by the propylene. The results showed that the S_N2-like concerted mechanism is the most favorable, with an activation energy of 9.5 kcal/mol. The transition state for this mechanism is shown in Figure 3. The bond lengths in the transition state are: Ti-O (2.44 Å), O-O (2.10 Å), O-H (1.69 Å), and C-O (2.36 Å).

corresponding to transition-state geometries (2) and (4), respectively, as shown in Figure 4a. The oxygen from the Si–O–O–Ti species then inserts into the C=C double bond of the adsorbed propylene molecule ($\Delta E_{\text{act}} = 1.2$ kcal/mol), as shown in Figure 4b.

The last two mechanisms involve defect sites, based on a partial silanol nest model and a full silanol nest model, respectively. As Figure 2 shows, a Ti site with one defect neighbor means a total of three neighboring hydroxyl groups (or silanol groups, Si–OH). In the partial silanol nest model, only one Si–OH group is modeled instead of three, and the epoxidation mechanism mentioned above is studied, with the transition-state geometry shown in Figure 3 [32]. In the full silanol nest model, the formation of a hydroperoxy intermediate (Ti–OOH) overcomes an activation barrier of 8.9 kcal/mol (Gibbs free energy at 298 K), with the transition-state structure shown in Figure 5a. Once the generated H₂O is removed from the active site, propylene can adsorb and react with the active Ti–OOH species. The activation energy for the transition-state structure (Figure 5b) is only 4.6 kcal/mol (Gibbs free energy at 298 K). In comparison to a partial silanol nest model, the Ti/defect site pathway with a full silanol nest is energetically more favorable with regard to the propylene epoxidation in the H₂O₂/TS-1 or H₂/O₂/Au/TS-1 catalytic systems.

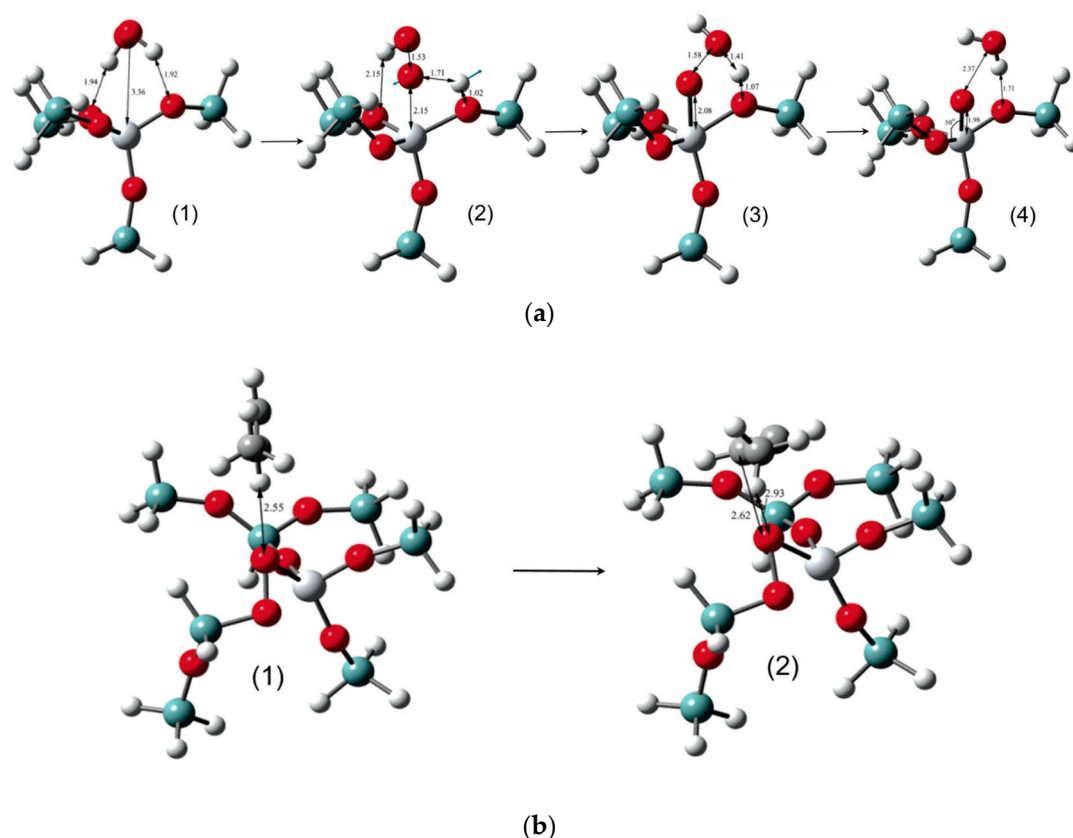


Figure 4. Murakami et al. mechanism: (a) the formation of SSiOOCTi species, where (1) is the preadsorbed complex of H₂O₂ on TS-1, (2) is the transition-state geometry for the first step in oxygen insertion to the peroxy intermediate on the closed Ti site, (3) is the stable intermediate geometry prior to the second step in oxygen insertion to the peroxy intermediate, and (4) is the transition-state geometry for the second step in oxygen insertion to the peroxy intermediate; (b) propylene epoxidation: (1) propylene adsorbed on the Ti site, and (2) is the transition-state geometry during the propylene epoxidation [164]. Distances are in Ångströms. Copyright © 2006 American Chemical Society.

The last two mechanisms involve defect sites, based on a partial silanol nest model and a full silanol nest model, respectively. As Figure 2 shows, a Ti site with one defect neighbor means a total of three neighboring hydroxyl groups (or silanol groups, Si–OH). In the partial silanol nest model, only one Si–OH group is modeled instead of three, and the epoxidation mechanism mentioned above is studied, with the transition-state geometry shown in Figure 3 [32]. In the full silanol nest model, the formation of a hydroperoxy intermediate (Ti–OOH) overcomes an activation barrier of 8.9 kcal/mol (Gibbs free energy at 298 K), with the transition-state structure shown in Figure 5a. Once the generated H₂O is removed from the active site, propylene can adsorb and react with the active Ti–OOH species. The activation energy for the transition-state structure (Figure 5b) is only 4.6 kcal/mol (Gibbs free energy at 298 K). In comparison to a partial silanol nest model, the Ti/defect site pathway with a full

silanol nest is energetically more favorable with regard to the propylene epoxidation in the $\text{H}_2\text{O}_2/\text{TS-1}$ catalytic systems.

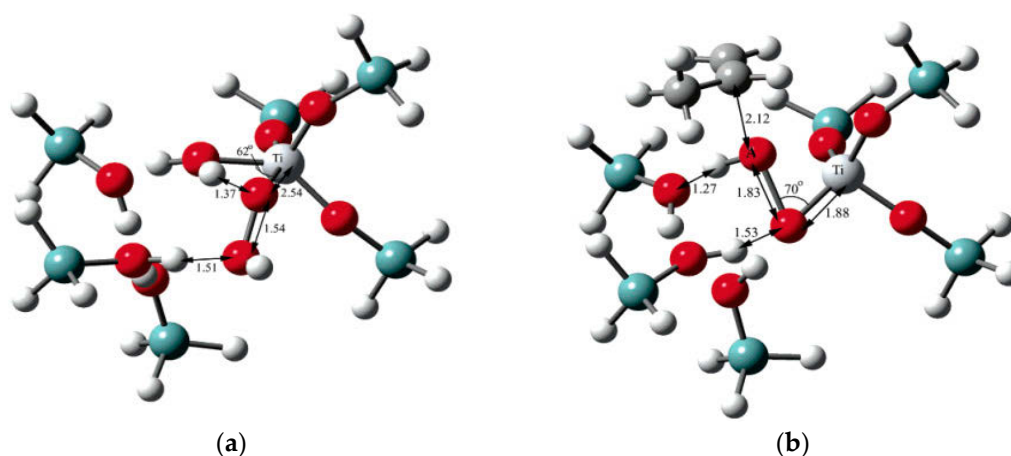


Figure 5. Ti/Ti-defect mechanism for the full silanol system: (a) transition state geometry for the formation of the hydroperoxy intermediate on the Ti site of TS-1, and (b) transition state geometry for propylene epoxidation [110]. Distances shown are in units of angstroms. Copyright © 2006 American Chemical Society.

Recently, Song's group performed DFT calculations to investigate the propylene epoxidation mechanism (stepwise and concerted mechanisms) with H_2O_2 over tripodal and Ti/defect (a full silanol nest model) sites, respectively (both tripodal and Ti/defect represent two types of internal Ti active sites) [109]. It was found that, on tripodal sites, both stepwise (through a three-membered ring (3MR) $\text{Ti}-(\eta^2\text{-OOH})$) and concerted (through a five-membered ring (5MR) $\text{Ti}-(\eta^1\text{-H}_2\text{O}_2)$) mechanisms are possible because of comparable barriers. On the other hand, over the Ti/defect site, both stepwise mechanisms are feasible either via a 3MR $\text{Ti}-(\eta^2\text{-OOH})$ or a 5MR $\text{Ti}-(\eta^1\text{-OOH})$ intermediate, and the concerted mechanism proceeds through a 5MR $\text{Ti}-(\eta^1\text{-H}_2\text{O}_2)$ intermediate. Among them, the stepwise mechanism via the 5MR $\text{Ti}-(\eta^1\text{-OOH})$ intermediate over the Ti/defect site is kinetically most favorable by comparison of the energy barriers of various pathways. Their studies indicate that both $\text{Ti}-\text{OOH}$ and $\text{Ti}-\text{H}_2\text{O}_2$ species are probably responsible for propylene epoxidation to produce PO.

5.2. Reaction Mechanism on Gold

In addition to the aforementioned reaction mechanisms on TS-1 in which propylene attacks active $\text{Ti}-\text{OOH}$ (or $\text{Ti}-\text{H}_2\text{O}_2$) species, recent DFT studies in combination with Fourier transform infrared (FTIR) spectroscopy have identified the adsorption of propylene and PO on the Au/TiO₂ catalyst interface [110,111]. Propylene was found to bind to a single atomic Au atom site via a ($\pi\sigma$)-interaction and bind to the TiO₂ surface via a π -interaction, and this interaction is also distinguishable through the C=C bond stretching frequency of propylene (Figure 6). The results reveal that the propylene-Au (particularly low coordinated Au atoms, e.g., corner and edge sites) interaction has a stronger binding energy in comparison to the propylene-TiO₂ interaction, suggesting a possible epoxidation route to form PO on Au particles. Friend et al. also investigated the adsorption of propylene on an Au(111) surface, and the adsorption strength was found to follow the trend: defect-free < vacancy < step < adatom [30], indicating that the low coordinated Au sites (e.g., step and adatom) can activate propylene to some extent.

When referring to the olefin epoxidation process, the most commonly assumed mechanism involves the formation of an oxametallacycle intermediate. For example, ethylene epoxidation on Ag(111) to produce ethylene oxide (EO) is considered to undergo an oxametallacycle intermediate, namely, OMME (oxygen-metal-metal-ethylene, a five-member ring) or OME (oxygen-metal-ethylene, a four-member ring) [112–114]. These oxametallacycle complexes have been experimentally identified on the silver surface [115–117]. The OME complex with a single Ag atom in its ring is suggested to be much more selective toward EO formation. In contrast, the OMME intermediate with two Ag atoms incorporated preferably supports acetaldehyde production [118].

based catalysts [121–125]. Moreover, OMMP (from $C_3H_6 + O$) will preferentially react to form propanal (from OMMP1) or acetone (from OMMP2) via a 1,2-H shift reaction instead of PO. At the same time, Moskaleva took into account an OMP (oxygen-metal-propylene, a four-member ring) species as a possible oxametallacycle intermediate incorporating one Au atom, and they found that the ring closure of OMP to form PO (epoxide) is less favored, as compared to its isomerization into propanal or acetone. Thus, the formation of acrolein, propanal, and acetone explains the low selectivity of PO on the bulk gold surface. In which the atomic O is bound to the middle C of propylene and the end C of C-C is linked to gold surface as demonstrated in Figure 8. Both OMMP1 and OMMP2 can evolve to the final product PO and OMMP1 is a possible intermediate to propanal. However, results show that the formation of OMMP is hindered and the reaction thermodynamically favored OMMP1 is easily isomerized to acetone or propanal by the abstraction of OMMP allylic hydrogen, leading to a more rational and propylene to PO is favored higher energy barrier than that by O, leading to less acrolein.

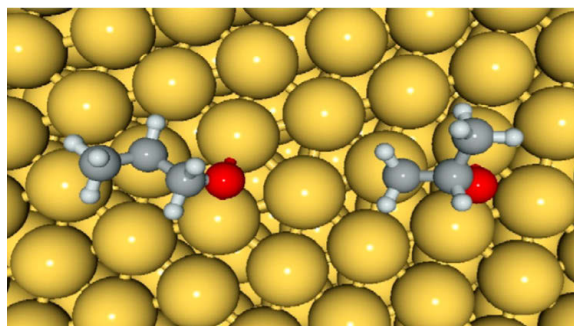


Figure 8. Structures of oxametallacycle intermediates OMMP1 (left) and OMMP2 (right) on the Au(111) surface. Copyright © 2009 Elsevier B.V.

The results from PO production are consistent with Moskaleva's study on Au(111) in which the stripping of the methyl hydrogen of propylene by atomic O to yield allyl was found to be the leading step of the reaction, and the allyl or acrolein or PO is the final product. On the other hand, Au(111) and this is mainly a gold surface for the partial oxidation of propylene, and it is a good catalyst for the oxidation of propylene to propanal or acetone [121, 125]. Moreover, OMMP1 (from 26–128) can preferentially react to form propanal (from OMMP1) or acetone (from OMMP2) via a 1,2-H shift reaction instead of PO. At the same time, Moskaleva took into account an OMP (oxygen-metal-propylene, a four-member ring) species as a possible oxametallacycle intermediate incorporating one Au atom, and they found that the ring closure of OMP and form PO (epoxide) is less favored, as compared to its isomerization into propanal or acetone. Thus, the formation of acrolein, propanal, and acetone explains the low selectivity of PO on the bulk gold surface. Moreover, the H-abstraction of propylene is more reactive than the H-abstraction of propylene by O, leading to a more rational and propylene to PO is favored higher energy barrier than that by O, leading to less acrolein. In addition, the reaction mechanism of propylene epoxidation on a PO production over Au₂/O₂ Au₂(OO)₁ by formation of the allyl species is detected experimentally from a reaction with H₂O/O₂ mixtures (with the C₃H₆ conversion of 0.88% and a PO selectivity of 51%) and indicates the formation of allyl species from the reaction of H₂O/O₂ of Au₂. Although the Au₂ surface performance is not sufficient for commercial application, it does highlight the interesting mechanism of PO production [126, 128]. In addition, a study has reported the formation of PO from Au₂ and Au₂ on Au₂ and Au₂ on Au₂ for the Au₂/MgO(OH) species oxidation reaction [129]. The role of H₂O in propylene epoxidation on Au₂ particles has also been computationally explored. For instance, Chang et al. proposed a catalytic reaction mechanism of propylene epoxidation with an H₂O/O₂ mixture on Au₂. Many studies have used DFT calculations [130, 131] in propylene epoxidation with H₂O to form OH and O₂ species after their adsorption on Au with different sites and the generated O₂ species OMMP1 is the C₃H₆ and O₂ of the incoming propylene molecule to form a four-member ring (OMP) intermediate ($\Delta E_{act} = 19.13$ kcal/mol). Finally, PO is produced via a ring closure of OMP ($\Delta E_{act} = 13.15$ kcal/mol) and desorbs from the Au₃₈ cluster (Figure 9a). The other PO production pathway on the Au₃₈ cluster is not via the OMP intermediate but directly from $C_3H_6 + OOH \Rightarrow PO + OH$ ($\Delta E_{act} = 22.65$ kcal/mol, Figure 9a), which also occurs on the Au₁₀ cluster ($\Delta E_{act} = 19.03$ kcal/mol,

Figure 9b). In the later studies of Chang et al., they reported the reaction mechanism of propylene epoxidation with an $\text{H}_2\text{O}/\text{O}_2$ mixture over $\text{Au}_7/\alpha\text{-Al}_2\text{O}_3(0001)$, by means of DFT calculations and ab initio molecular dynamics (AIMD) simulations (leading to PO, acrolein, and propanol) and allylic hydrogen atom transfer of propylene for leading to acrolein. Al_2O_3 surface fluorine atoms (hydrogenation) and molecular O_2 mechanism of the reaction (adsorption of O_2 is a allylic hydrogen atom with H_2O adsorbed at the propylene interface active sites) are proposed. In contrast with the OMMP formation as a possible way for PO based DFT calculations using an AIMD as an oxidant. While in the OMMP mechanism, the PO selectivity is indicated to be due to the activation barrier for OMMP formation is. OMMP is stronger than that of the stripping of propylene to finally produce PO via the ring closure of the OMMP intermediate.

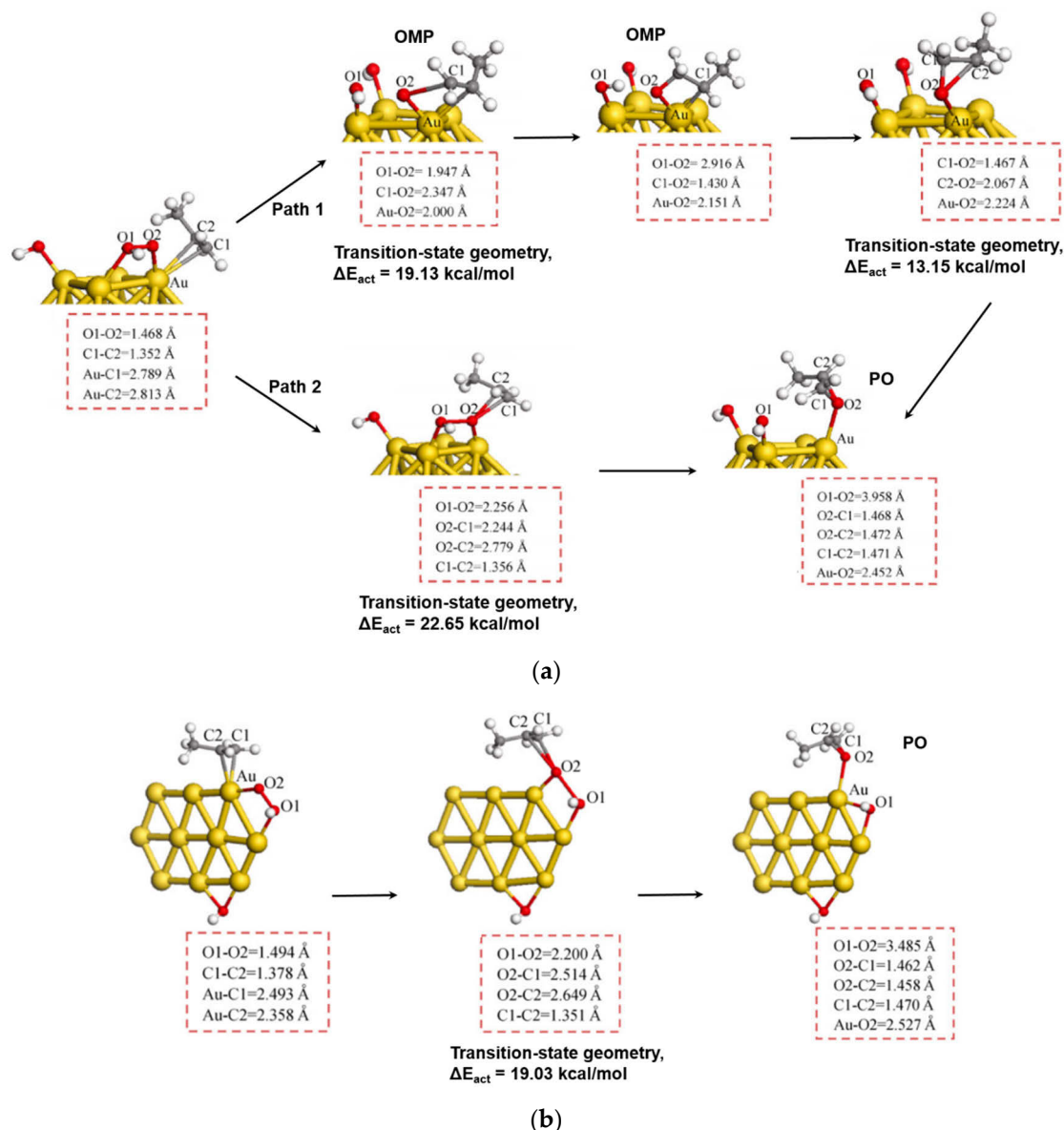


Figure 99. PO formation (a) on Au_8 cluster where two different pathways are shown with their corresponding transition state geometries and activation energies (b) on an Au_{19} cluster where only one path is possible along with the corresponding transition state geometry and activation energy. Copyright © 2011 Elsevier B.V.

5.3. Although many studies have indicated that the epoxidation of propylene using molecular oxygen is unlikely [11,30], Hu et al. demonstrated its possibility with DFT calculations on $\text{Au}(111)$, in which OMMP is derived from O–O bond cleavage of an oxametallacycle intermediate OOMMP [31]. Two key nondefect and defect Ti site in the form of $\text{Ti-H}_2\text{O}_2$ or further dissociate to form Ti-OOH species. Propylene then adsorbs around the Ti-OOH (or $\text{Ti-H}_2\text{O}_2$) species, followed by the epoxidation step, suggesting a “sequential” mechanism (H_2O_2 formation on Au nanoparticles first and then diffusion to Ti sites). Nonetheless, it was shown that propylene adsorption in TS-1 pores without any Au

competing reactions, OMMP formation (leading to PO, acrolein, and propanal) and allylic hydrogen stripping of propylene (leading to acrolein, CO₂, etc.), were compared via both atomic and molecular O₂ mechanisms. In the atomic O mechanism, allylic hydrogen abstraction is much easier to proceed with lower activation barriers, in contrast with OMMP formation, indicating a poor PO selectivity when using atomic O as an oxidant. While in the molecular O₂ mechanism, PO selectivity is enhanced since the activation barrier for OMMP formation is much lower than that of the stripping of methyl hydrogen.

5.3. Reaction Mechanism on Au/Ti Interface Sites

With regard to different mechanisms mentioned in Section 5.1, H₂O₂ species adsorb on the nondefect and defect Ti site in the form of Ti–H₂O₂ or further dissociate to form Ti–OOH species. Propylene then adsorbs around the Ti–OOH (or Ti–H₂O₂) species, followed by the epoxidation step, suggesting a “sequential” mechanism (H₂O₂ formation on Au nanoparticles first and then diffusion to Ti sites). Nonetheless, it was shown that propylene adsorption in TS-1 pores without any Au particles or clusters ($E_{\text{ads}} = -10.0$ kcal/mol) is significantly weaker than that on Au/Ti interface sites ($E_{\text{ads}} = -20.0$ kcal/mol) [133], which is consistent with the experimentally observed adsorption behavior [134,135]. Thus, the “simultaneous” mechanism (2-site) that does not require Ti–OOH and Ti–H₂O₂ species is proposed to proceed at the Au/Ti interfacial sites (it is actually OOH species on Au nanoparticles or H–Au–OOH species) [133]. In this mechanism, propylene molecules adsorbed on interfacial Ti sites will attack OOH or H–Au–OOH species formed on Au particles; thus, Ti plays an indirect role.

Although there are different opinions about the active sites for the epoxidation reaction, a reasonable proximity between Au and Ti sites is generally considered to be indispensable for the PO reaction, suggesting the existence of a well-defined reaction zone [110,111,133,135,136]. Previous experiments have indicated that the perimeters between Au particles and Ti sites are active for the epoxidation reaction [16,137], as well as several side reactions (isomerization and oxidative cracking, etc.) [25,138].

At a larger modeling scale, Turner’s group used kinetic Monte Carlo (KMC) simulations to investigate propylene epoxidation over an Au/TiO₂/SiO₂ catalyst. In their model, H₂O₂ is first generated from coadsorbed H₂ and O₂ on Au nanoparticles, and H₂O₂ can then either degrade into water or diffuse to TiO₂ sites supported on SiO₂ to epoxidize propylene molecules [139]. The PO formation rates predicted by KMC simulations are consistent with experimental reports corresponding to different temperatures and feed concentrations of O₂ [140]. In their later kinetic modeling studies [141], several key side reactions encountered during PO formation are taken into account (acrolein formation, propanal and acetone formation from OMP isomerization, oxidative cracking into CO₂, etc.), affecting the overall PO selectivity. According to Figure 10, it is the OOH species formed on Au nanoparticles that directly transfers to the neighboring Ti sites (interfacial Ti sites at the dual Au/Ti sites) to form active Ti–OOH species and epoxidize propylene to form an oxametallacycle OMP (OMC’ or OMC”, depending on which carbon of propylene is connected with O). Their KMC simulations closely reproduce the experimental findings [140]. For instance, it was found that the O₂ feed concentration has a slight effect on PO selectivity (since O₂ adsorption on Au particles is very weak), which is in good agreement with the kinetic tests of Taylor and Chen [142,143]. At the same time, both KMC simulations and experiments demonstrate that PO selectivity increases along with decreasing reaction temperature and increasing H₂/C₃H₆ feed concentration ratio, since low temperature and high H₂ feed concentration can help suppress side reactions that contribute to acrolein, propanal, acetone, CO₂, and ethanal. It seems that the synergy of the Au/Ti dual interface sites plays a central role in the reaction network of propylene epoxidation.

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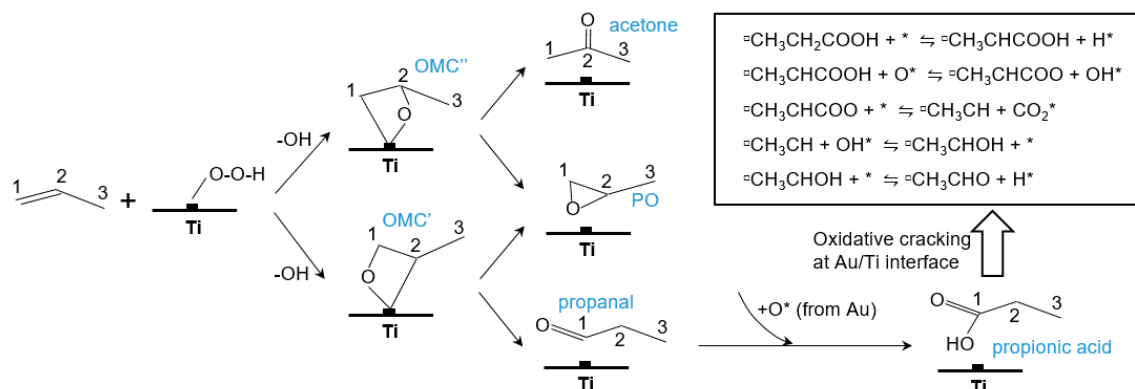


Figure 10. Reaction network at the Au/Ti interface. The * symbol represents a bare Au site, and □ represents a bare interfacial Ti site that is in contact with Au nanoparticles (for clarity, Au nanoparticle is not shown here). The species attached to * or □ indicates one Au surface-bound species or one Ti surface-bound species, respectively [141]. Copyright © 2018 Elsevier Ltd.

It is worth noting that, although low temperatures yield high PO selectivity, the propylene conversion is typically very low (<2%) [138,144]. Efforts to enhance propylene conversion by raising the reaction temperature inevitably lead to decreasing PO selectivity because of consecutive PO reactions (oligomerization, oxidative cracking). In particular, the oxidative cracking into acids and further into CO₂ is correlated with decarbonylation and decarboxylation of carboxylic acids [17,23–26]. However, only a few studies have investigated the role of carboxylic acid oxidation on Au-based catalysts [23,145–147]. The active sites were found to reside at the Au/TiO₂ interface, again highlighting the synergistic effect of interface sites in heterogeneous catalysis.

Matthew's group studied the partial oxidation of acetic acid by O₂ at the dual perimeter sites of an Au/TiO₂ catalyst using first-principle DFT calculations. They identified that a novel gold ketenylidene (Au₂=C=C=O) intermediate is formed from the deoxygenation of acetic acid [145,146]. The ketenylidene species is also identified by its measured characteristic stretching frequency $\nu(\text{CO}) = 2040 \text{ cm}^{-1}$ using in situ infrared spectroscopy. As a comparison, no ketenylidene formation was observed on Au/SiO₂ or a TiO₂ blank sample, suggesting the involvement of dual catalytic Ti⁴⁺ and Au perimeter sites. The production of CO₂ and H₂O is also observed when raising the reaction temperature to 473 K, due to the total oxidation of the ketenylidene species. The decarboxylation and decarbonylation of longer chain carboxylic acids at the Au/TiO₂ interface has also been investigated [23,147]. For instance, O₂ activation and the oxidation of propionic and butyric acids to form propionate and butyrate first proceed at the dual Au/TiO₂ interface. Dehydrogenation of propionate and butyrate to form acrylate and crotonate then occurs, followed by the further oxidation and the subsequent C–C and C–O cleavage to generate the Au₂=C=C=O intermediate. The formed ketenylidene species can be hydrogenated to produce H₂=C=C=O (g), which either readily desorbs from the catalyst surface or undergoes a full oxidation to form CO₂ and H₂O.

6. Conclusions and Perspectives

Direct gaseous-phase epoxidation of propylene over gold-based catalysts in the presence of H₂ and O₂ has been extensively studied using theoretical techniques. These studies have provided fundamental insights into H₂ and O₂ adsorption, H₂O₂ (OOH) species formation, and propylene epoxidation with gold-based catalysts. For realistic evaluation of propylene epoxidation, the large number of reaction species as well as the structural complexity of supported catalysts require detailed investigations of different reaction pathways on the various active sites, such as metal (gold), support (TiO₂, TS-1, etc.), and the metal/support interface. As the reaction proceeds, changes in the composition of surface species usually take place and may influence catalytic activity. Capturing the dynamic behavior of catalytic surface is challenging and herein KMC simulations aid to detect possible

reaction events “on the fly” and prove significant to explicitly capture the temporal evolution of the catalytic system. On the other hand, it demands that the validation of the KMC results in a detailed comparison of experimental findings, and underscores the need for methods able to quantify the effect of the uncertainty of certain parameters toward simulation results. Additionally, in complex systems, sensitivity analysis is essential to identify the main parameters influencing the observed behaviors and characterize such influences.

Until now the reaction mechanism toward propylene epoxidation over Au/titania/silica is still debated, and the most convincing one is based on the synergy between Au particles and isolated tetrahedral titanium (or titania), where hydroperoxyl species (OOH or H_2O_2) is formed on Au nanoparticles first, and then transfers to the adjacent Ti sites to form an active Ti–OOH intermediate, followed by the epoxidation of propylene to produce PO. In this process, some byproducts are coproduced at the Au/support interface and lead to catalyst deactivation. Additionally, a higher propylene conversion level (>10%) and higher hydrogen efficiency (>50%) will be essential for a commercial process to be profitable.

It is known that H_2O_2 is a weak acid, and as suggested in our previous studies [141], Brønsted acid-functionalized supports may promote OOH spillover, thereby enhancing the probability of OOH transferring to the neighboring Ti sites. This would potentially reduce OOH decomposition to O on the Au surface, leading to more PO production. Additionally, it is proposed that bimetallic alloys (e.g., Au–Pd and Au–Ru) or trimetallic alloys (e.g., Au–Pd–Ru) supported on TiO_2 can be highly active for H_2O_2 production, since this leads to a significant synergistic enhancement in activity (from Pd and Ru) and selectivity (from Au) [148–151]. Thus, such Au–Pd, Au–Ru, and Au–Pd–Ru alloy nanoparticles loaded on TS-1 support may lead to improved propylene conversion, as well as improved hydrogen utilization efficiency. In addition to Ti-based supports, other reducible support candidates (such as CeO_2 , Fe_2O_3 , and Co_3O_4) need to be theoretically explored, since they can help anchor Au nanoparticles to some extent and promote O_2 adsorption and activation at the interfacial sites [16,53,152–154]. Improved computational approaches will enable the modeling of multifunctional catalysts, created by multicomponent nanoparticles deposited on supports. These theoretical models can lead to more efficient prediction of advanced catalysis by building a fundamental understanding on active sites of multicomponent nanoparticles, multiple interfaces, and intermediate transfer.

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