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Prospect of vapor phase catalytic H₂O₂ production by oxidation of water

Mayfair C. Kung, Harold H. Kung *

Chemical and Biological Engineering Department, Northwestern University, Evanston, IL. 60208, United States

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ABSTRACT

Vapor phase catalytic hydrogen peroxide production by oxidation of water is possible by coupling the reaction with oxidation of an organic sacrificial reductant. It is potentially a safer process than direct synthesis from H₂ and O₂. Based on mechanistic information available mostly for liquid phase catalytic processes, feasible reaction mechanisms for such coupled reactions are proposed based on which desirable catalyst properties are identified. It is found that the surface-adsorbed oxygen bond is an important parameter for identifying desirable catalysts. Thermodynamics can be used to identify the types of organic oxidation reactions that can couple with water oxidation such that H₂O₂ formation becomes thermodynamically favorable. Reactions such as epoxidation of alkenes and selective oxidation of alkanes to alcohols cannot provide sufficient thermodynamic driving force, whereas oxidation of alcohols to aldehydes and to acids can. Finally, further research is suggested to identify catalytic properties important for H₂O₂ decomposition and for coupling selective oxidation of organic compounds to oxidation of H₂O in order to facilitate development of H₂O₂ production coupled with selective organic oxidation.

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1. Introduction

Hydrogen peroxide (H₂O₂) has found wide applications in industry. For example, it is a selective oxidant for the production of fine chemicals such as epoxides, bleaching agent in paper pulp production, a disinfectant, and a water purification agent. Industrial production of H₂O₂ is mainly by liquid phase autooxidation of anthraquinone, which is a free-radical process [1]. H₂O₂ can also be produced by autooxidation of other organic compounds, and an obsolete industrial process involved autooxidation of 2-propanol [1,2].

The formation of H₂O₂ in the liquid phase accompanying catalyzed oxidation of organics has been reported nearly two decades ago. H₂O₂ was detected by titration during palladium (II) acetate-catalyzed oxidation of terminal alkenes to ketones

in an organic solvent [3,4]. Its formation as the initial production of dioxygen reduction was implied in the Pd acetate-catalyzed 2-octanol oxidation from the stoichiometric consumption of molecular O₂ and 2-octanol [5]. H₂O₂ formation during aqueous phase oxidation of glycerol catalyzed by Au/C [6] and oxidation of CO catalyzed by Au/TiO₂ [7] and Au/Calgon [8] have been reported. Although these reports demonstrated that it is technically feasible to produce H₂O₂ by aqueous phase oxidation of organics or CO, the need to separate the organics and the soluble catalysts from the mixture can be expensive and poses a hurdle to commercialization.

Direct catalytic oxidation of H₂ with O₂ to form H₂O₂ in the vapor phase would be the most desirable, and it has been demonstrated in laboratories [9–11]. However, the process has not been commercialized due to concern for safety since effi-

* Corresponding author. E-mail: hkung@northwestern.edu

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cient production involves H_2 and O_2 present as an explosive mixture. This concern for safety could be mitigated by using another reductant instead of H_2 , such as organics. In this article, we offer a perspective of the feasibility of vapor phase production of H_2O_2 by simultaneous catalytic oxidation of organics by examining postulated reaction mechanisms and deriving from them what would be essential properties of a solid catalyst.

2. Mechanisms for liquid phase formation of H_2O_2

With the exception of direct formation of H_2O_2 from H_2 and O_2 and from autooxidation of anthraquinone, all available mechanistic information for H_2O_2 production are derived from investigations of liquid phase oxidation of organic compounds where the emphasis is on the mechanism of the organic reaction. Formation of H_2O_2 in the anthraquinone autooxidation process involves first the hydrogenation of anthraquinone to anthrahydroquinone. The H atom of the OH group in anthrahydroquinone is abstracted by an O_2 molecule to form a $\cdot\text{O}_2\text{H}$ radical (Scheme 1). Abstraction of another H atom from another OH group by the $\cdot\text{O}_2\text{H}$ radical completes the formation of H_2O_2 and regenerates the anthraquinone [12]. For the H_2O_2 formation during alcohol or aldehyde oxidation catalyzed by metal complexes such as Pd acetate, O_2 is activated on the metal complex by forming a peroxy ligand (Scheme 2). Insertion of the proxy into a metal-hydride bond forms a hydroperoxy ligand [13,14]. Hydrogenation or hydrolysis of the metal-hydroperoxy bond results in H_2O_2 formation [15].

The mechanism of H_2O_2 formation during aqueous Au-catalyzed oxidation of glycerol and CO can be inferred from the isotopic labelling of the organic products when ^{18}O -labeled O_2 or H_2O was used in the reaction. In glycerol oxidation, ^{18}O was found in the glyceric acid product only when H_2^{18}O was used but not with $^{18}\text{O}_2$ [6]. In contrast, in the Au-catalyzed CO oxidation-assisted formation of peroxide which was subsequently used to form propylene epoxide, ^{18}O -labelled propylene epoxide was observed exclusively when $^{18}\text{O}_2$ was used but not with H_2^{18}O [7]. These results are consistent with the mechanism shown in Scheme 3 [6]. O_2 is activated by associative adsorption, possibly as a peroxy species not unlike that in Scheme 2. It is then hydrogenated to form hydroperoxy, and eventually to H_2O_2 . It should be noted that in Scheme 3, the catalytic cycle is not complete until the adsorbed hydroxyl ($\cdot\text{OH}$) is removed

from the surface. In the CO oxidation-assisted process, the hydrogen source is H_2O , and the reaction of CO with $\cdot\text{OH}$, similar to steps in the formation of adsorbed formate in the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$), completes the catalytic cycle and accounts for the appearance of labelled CO_2 when H_2^{18}O was used but not with $^{18}\text{O}_2$ [7]. In the glycerol oxidation-assisted process, the removal of $\cdot\text{OH}$ was proposed to be accomplished by acquiring an electron to form hydroxyl anion (OH^-) that desorbs into the liquid phase [6].

3. Formation of H_2O_2 in vapor phase catalytic processes without added H_2

Without added H_2 , another hydrogen source is needed to hydrogenate O_2 . It would be ideal if H_2O can serve as the hydrogen source. However, direct oxidation of H_2O with O_2 (Eq. (1)) is thermodynamically uphill ($\Delta G_{\text{Eq. (1)}}^0 = 116.7 \text{ kJ/mol}$). Thus a source of energy is needed to drive the reactions forward.

Light is the most commonly utilized energy source for H_2O_2 and $\cdot\text{OH}$ production, and photocatalytic processes have been heavily studied and reviewed. Known photochemical methods generally have very low overall energy utilization efficiencies, since the theoretical (i.e. minimum) light energy required for this two-electron (i.e. two photon) process of Eq. (1) is 0.6 eV per photon, but a typical photocatalytic process utilizes UV light (e.g. 3.1 eV at 400 nm) that corresponds to a theoretical maximum energy efficiency of 20%. Even for process under development that utilizes visible light (e.g. yellow light of $\sim 2.14 \text{ eV}$ at 580 nm), the theoretical efficiency is only 29%. The actual energy efficiency is significantly less than 10% due to less than perfect quantum efficiencies and energy losses in the transfer of excited electron to surface species, as well as losses incurred with successive steps in the reaction sequence leading to peroxide formation. Furthermore, these processes demand reactors designed for maximum light exposure, efficient mixing, and thermal control.

Another source of energy that can be supplied to effect Eq. (1) is energized electrons from applied electrical potential. Although electrocatalysis is well established, process economics, energy utilization efficiency, and process complexity are barriers to their wide applications. Loss of energy efficiencies are due to the overpotential needed to activate the oxygen molecule, losses due to the competing reaction of electrolysis of water, and to the decomposition of the formed peroxide on the electrode surface.

Another approach is to make use of the widely practiced strategy in the chemicals and fuel processing industry, which is to couple reactions thermally, i.e. using heat released in one reaction to drive another independent reaction. This practice is highly inefficient, energy intensive, and costly for dilute streams since most of the energy is expended in heating up very large quantities of diluent instead of being utilized to advance the desired reaction.

On the other hand, coupling of reactions at the elementary steps would be more desirable and energy efficient. However,

there are few systematic studies of such coupled reactions. Thus, they represent a potential area of fruitful research. Among the few literature examples of coupling chemical reactions to achieve production of H_2O_2 in an aqueous medium is the coupling of CO oxidation to CO_2 with the formation of H_2O_2 using a Au catalyst mentioned earlier [8]. ^{18}O -isotope labelling experiments indicated that the oxygen atoms in the peroxide are derived from the O_2 molecule, whereas those in CO_2 are derived from CO and H_2O [7]. Although the CO utilization efficiency is very low, as a majority of CO is oxidized to CO_2 without being coupled to water oxidation, the molecule serves as the sacrificial reductant and its oxidation to CO_2 provides the thermodynamic driving force.

In addition to CO, it is useful to consider what other compounds could serve as sacrificial reductants. Of particular interest would be organic compounds that could be oxidized to useful/valuable products and co-produced with H_2O_2 . To this end, one can use thermodynamics to gauge the feasibility of the coupled reactions as to whether the organic oxidation reactions can provide sufficient thermodynamic driving force to effect H_2O_2 formation from H_2O and O_2 . Table 2 shows the $\Delta G^\circ_{\text{rxn}}$ of oxidation of different classes of organics. Compared with $\Delta G^\circ_{\text{Eq.(1)}}$ of 116.7 kJ/mol for Eq. (1), it is clear that most oxidation reactions meet the minimum thermodynamic requirement, except epoxidation of alkenes. However, thermodynamics determines what can be achieved potentially without regard to reaction rates, and reaction mechanisms are needed for reaction kinetics discussion. Since coupling these reactions with H_2O_2 in the vapor phase has not been demonstrated yet, we will extrapolate the knowledge collected for the liquid phase reactions and postulate some feasible mechanisms for discussion, as illustrated below with alcohol oxidation.

Fig. 1 shows three possible mechanisms of alcohol oxidation to aldehyde coupled to H_2O_2 formation. Mechanism A is analogous to Scheme 2 in which an adsorbed peroxy species is formed when O_2 is adsorbed onto a catalyst, which is then hydrogenated to H_2O_2 while the alcohol is dehydrogenated to aldehyde. Although this process is thermodynamically feasible ($\Delta G^\circ_{\text{rxn}} \approx -70$ kJ/mol), it requires the unlikely formation of adsorbed H atom by cleaving a C–H bond in the alcohol in the presence of O_2 (or adsorbed O). Instead, it should be more likely that breaking of such a C–H bond is facilitated by adsorbed O via formation of a surface *OH , as in Mechanism B.

In mechanism B, O_2 is adsorbed as a surface peroxy species, which is hydrogenated by H transfer from an adsorbed H_2O (VI $\rightarrow$ VII). The presence of H_2O was found to be necessary in H_2O_2 formation during methanol oxidation using a Au catalyst, implying its involvement in the reaction mechanism [7]. A varia-

Fig. 1. Possible mechanisms for gas-phase H_2O_2 formation during catalytic alcohol oxidation. Mechanisms B and C are more probable than A.

tion of this step is that the H is transferred from an adsorbed hydroxyl (*OH). Further hydrogenation from another hydroxyl results in H_2O_2 . Leaving behind an adsorbed O (VIII). This adsorbed O is consumed in the oxidative dehydrogenation of the alcohol (VIII $\rightarrow$ IX $\rightarrow$ V).

In Mechanism C, O_2 is activated by adsorption onto a surface oxygen vacancy (v in X), which significantly weakens the O–O bond. Cleavage of this bond and insertion of its O into a surface *OH results in a surface peroxy (XII), which is hydrogenated to H_2O_2 . The O atom that is left in the vacancy is consumed in the alcohol oxidation (XIII $\rightarrow$ XIV $\rightarrow$ X) to regenerate the vacancy.

Additional experimental data will be needed to test the validity of these mechanisms. Nonetheless, at this point, one may use these postulated mechanisms to develop guidelines for catalysts that might be suitable for the generation of H_2O_2 during oxidation of an organic compound. Upon examining the two more likely mechanisms B and C, a common feature becomes apparent: the need to remove the O atom left on the catalyst surface in the process of H_2O_2 formation. In mechanism B, this residual atom is an adsorbed O (VIII), and in mechanism C, it is a lattice O (XIII), and they are removed by reaction with the sacrificial organic reductant. Thus, the minimum $\Delta G^\circ_{\text{rxn}}$ of the oxidation reaction of the sacrificial reductant must be sufficient to compensate not only the $\Delta G^\circ_{\text{Eq.(1)}}$ but also the energy ($\Delta G^\circ_{\text{*O}}$) associated with removal of the residual O (denoted *O). Fig. 2 show this minimum $\Delta G^\circ_{\text{rxn}}$ needed, which is equal to the sum of $\Delta G^\circ_{\text{*O}}$, the kinetic barrier for the removal *O (i.e. that barrier to form *O^TS) $\Delta G^\circ_{\text{barrier}}$, and $\Delta G^\circ_{\text{Eq.(1)}}$.

Table 2

$\Delta G^\circ_{\text{rxn}}$ of oxidation reactions ($\text{R} + 0.5\text{O}_2 = \text{RO}$).

Reaction	$\Delta G^\circ_{\text{rxn}}$, kJ/mol
Alkane to alcohol	~ -140
Primary alcohol to aldehyde	~ -200
Aldehyde to acid	-250 to -260
Alkene to epoxide	~ -115
CO to CO_2	-222

Fig. 2. Energy diagram showing the minimum requirement for H_2O_2 formation for mechanism B. * is the active site, *O is surface site with an adsorbed oxygen, *O^{TS} is the transition state for the step of removal of adsorbed O.

Fig. 3. Figure showing the thermodynamic requirements of coupling oxidation of organics with the reaction of H_2O oxidation by O_2 to form H_2O_2 . The y-axis is the energy required to remove the residual O $\Delta G^\circ_{\text{o}}$ plus the energy of H_2O oxidation $\Delta G^\circ_{\text{Eq},1}$. The slanting lines are for different values of $\Delta G^\circ_{\text{barrier}}$, which is the kinetic barrier for removal of residual O. Also shown are the approximate values of $\Delta G^\circ_{\text{rxn}}$ for classes of organic compounds taken from Table 2.

Table 3
Estimates of Metal–Oxygen Bond Strengths.

	Heat of dissociate adsorption of H_2O , ^a kJ/mol H_2O	Heat of formation of oxide, ^b kJ/mol oxide	Heat of formation, ^c kJ/mol metal	#M–O bond per metal ^d	Heat of formation per metal–O bond, ^e kJ/mol
$\alpha\text{-Cr}_2\text{O}_3$	–121.0	–1134.7	–567.4	6.0	–94.6
Fe_3O_4	–94.0	–1120.9	–373.6	5.3	–70.5
Fe_3O_4	–101.0	–1120.9	–373.6	5.3	–70.5
Fe_3O_4	–111.0	–1120.9	–373.6	5.3	–70.5
Fe_2O_3	–118.0	–825.5	–412.8	6.0	–68.8
Fe_2O_3	–130.0	–825.5	–412.8	6.0	–68.8
ZnO	–104.0	–350.5	–350.5	4.0	–87.6
ZnO	–157.0	–350.5	–350.5	4.0	–87.6
$\alpha\text{-Al}_2\text{O}_3$	–138.0	–1675.7	–837.9	6.0	–139.6
CaO	–170.0	–635.1	–635.1	6.0	–105.9
MnO	–68.0	–91.9	–91.9	6.0	–15.3
SiO_2	–160.0	–905.5	–905.5	4.0	–226.4
TiO_2 anatase	–145.0	–940.0	–940.0	6.0	–156.7
TiO_2 rutile	–125.0	–939.0	–939.0	6.0	–156.5

^a From Enthalpies and Entropies of Adsorption on Well-Defined Oxide Surfaces: Experimental Measurements, See Ref. [24].

^b From NIST Webbook SRD69, Condensed phase thermochemistry data, assessed July 2018.

^c Equals heat of formation per mole of oxide divided by mole metal per mole oxide.

^d Coordination number of metal in the bulk oxide.

^e Equals heat of formation per mole of metal in the oxide divided by the metal coordination number.

Fig. 3 summarizes these considerations for the case of removal of adsorbed O, plotting the sum of $\Delta G^\circ_{\text{o}}$, $\Delta G^\circ_{\text{barrier}}$, and $\Delta G^\circ_{\text{Eq},1}$ versus $\Delta G^\circ_{\text{rxn}}$ for the reaction of the sacrificial reductant. The dotted horizontal line at 116.7 kJ/mol is the thermodynamic minimum required to overcome the $\Delta G^\circ_{\text{Eq},1}$. Any energy needed to overcome the kinetic barrier ($\Delta G^\circ_{\text{barrier}}$) and to break the surface-oxygen bond ($\Delta G^\circ_{\text{o}}$) will be addition to that. The three sloping lines represent three $\Delta G^\circ_{\text{barrier}}$ of 10, 30, and 50 kJ/mol, respectively, and various values of $\Delta G^\circ_{\text{o}}$. A point on these lines corresponds to the situation when:

$$\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_{\text{Eq},1} + \Delta G^\circ_{\text{barrier}} + \Delta G^\circ_{\text{o}}$$

Thus, points to the left of these lines correspond to cases when the energy of oxidation of the sacrificial reductant is insufficient to overcome the ($\Delta G^\circ_{\text{Eq},1} + \Delta G^\circ_{\text{barrier}} + \Delta G^\circ_{\text{o}}$) requirement for catalytic H_2O_2 production for that catalytic system. On the other hand, points to the right of these lines correspond to catalytic systems that are feasible. This analysis shows that for practical purposes, it is difficult to use hydrocarbon molecules effectively as sacrificial reductant for H_2O_2 production. Alcohols and aldehydes should be more effective. The analysis also provides guidelines for the choice of catalysts by providing constraints for strength of adsorption of O. In general, catalysts with low binding energy of O is preferable. Thus, the weak binding energy of O on Au makes Au a good catalyst choice. Other candidates include various metal oxides such as Fe, Cu, Mn, Zn, and Cr oxide, according to the data in Table 3. The conclusion that catalysts of weaker surface–oxygen bond is desirable is similar to that arrived for electrochemical production of H_2O_2 [16].

The discussion thus far focuses on the production of H_2O_2 as the primary product. For an economically viable industrial process, it is also necessary to produce H_2O_2 at high concentrations with minimal consumption of sacrificial reductant. These demand additional requirements on the catalyst not discussed

here, which include catalysts to have low activity in decomposing H_2O_2 (into H_2O and O_2) but high selectivity in oxidizing the sacrificial reductant to a selective oxidation product (such as alcohol to aldehyde but no further). For a long time, researchers have investigated the desirable catalytic properties for selective oxidation of hydrocarbons, but none has addressed the coupled production of H_2O_2 . Thus this can be a new and fruitful direction of research.

4. Electrogenative H_2O_2 production

Fig. 3 identifies organic oxidation reactions that can be used to produce H_2O_2 . The ΔG° of the coupled processes is thermodynamically favorable. In principle, for these coupled processes, it is possible to also derive useful work from them. One such method is to couple these reactions electrochemically. Although such processes need to be in the liquid phase, they are included for discussion because of the potential high overall energy efficiency. Thus, oxidation of the reductant (e.g. alcohol) can occur at an anode where protons and electrons are produced (Eq. (2)). At the cathode, the electrons reduce O_2 , and the reduced O_2 combines with protons to form H_2O_2 (Eq. (3)), and the overall reaction is the oxidation of the reductant with the formation of H_2O_2 . The available work in the overall reaction can be captured as electrical work.

Although such an electrogenerative concept has been known for a long time and is the basis of fuel cell operations [17,18], its potential for H_2O_2 generation has not been extensively studied.

Recently, there is emerging interest in using microbial bioelectrochemical systems (BESs) such as Microbial Fuel Cells (MFCs) and Microbial Electrolysis Cells (MEC) that use microorganisms as catalysts to oxidize organic compounds at the anode of the electrogenerative cell. Use of a microbial fuel cell to generate H_2O_2 was first reported about a decade ago using acetate oxidation to bicarbonate to provide the thermodynamic driving force [19]. Since then, other reactions have been used successfully, including glucose oxidation [20].

There are analyses to determine requirements for optimal electrocatalysts [21]. Monometallic, bimetallic, organic semi-

conductor [22], oxidic, and N-doped C electrodes are known to produce H_2O_2 rather selectively [21,23]. The reactions at the electrode surfaces are:

where * denotes a surface adsorption site. Thus, the reaction rate depends on the binding strength of hydroperoxy (*-OOH) [21]. For surfaces where the binding strength is too weak such as on Au and Pd/Au, formation of *-OOH is limiting; whereas for surfaces where the binding is too strong such as Pt and Pd, degradative dissociation of *-OOH limits H_2O_2 formation.

5. Conclusions

In this article, the feasibility of a vapor phase catalytic H_2O_2 production process by coupling the oxidation of water with the oxidation of an organic compound is analyzed. Consideration of the thermodynamics of the reactions involved provides constraints that determine which organic reactions are useful. By postulating feasible reaction mechanisms, we further discussed the challenges of identifying a suitable catalyst that would promote the reaction at an adequate rate. The result of the analysis identified metal-oxygen bond strength to be a useful parameter for high activity. In general, catalysts with stronger metal-oxygen bonds require more thermodynamically favorable (more negative $\Delta G^\circ_{\text{rxn}}$) organic oxidation reactions to couple with the H_2O oxidation reaction. Undoubtedly, this generalization is subjected to refinement by taking into account variations in parameters that are assumed constant or estimated with simplified assumptions, especially the various bond energies, but the generalization arrived here may serve as a starting point in search of suitable catalysts. The analysis also identified potentially fruitful research directions. One is to expand our understanding of desirable catalytic properties for selective oxidation of hydrocarbons to include the requirement for coupled production of H_2O_2 , and another to understand the requirement to minimize H_2O_2 decomposition activity of a catalyst without negatively impacting its H_2O_2 formation activity.

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Graphical Abstract

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Mayfair C. Kung, Harold H. Kung*
Northwestern University, USA

Efficient coupling of some catalytic organic oxidation reactions with oxidation of water by molecular oxygen enables production of hydrogen peroxide.

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气相催化水氧化制备H₂O₂的展望

Mayfair C. Kung, Harold H. Kung *

西北大学化学与生物工程系, 埃文斯顿60208, 伊利诺斯州, 美国

摘要: 通过与有机牺牲还原剂氧化反应耦合, 可以实现气相催化水氧化生产过氧化氢. 该过程可能是比直接从氢气和氧气合成更安全. 基于现有大多数的液相催化反应机理, 提出了该耦合反应可行的反应机理, 并在此基础上确定了理想的催化剂性能. 结果表明, 表面吸附氧键是识别理想催化剂的重要参数. 热力学可以用来确定有机氧化反应的类型, 这种氧化反应可以与水氧化反应耦合, 从而使H₂O₂的生成是热力学有利反应. 诸如烯烃环氧化和烷烃选择性氧化等反应不能提供足够的热力学驱动力, 而醇氧化为醛和酸则可以. 最后, 建议进一步研究确定对H₂O₂分解和有机化合物选择性氧化与H₂O氧化耦合反应重要的催化性能, 以促进与选择性有机氧化耦合合法生产H₂O₂的发展.

关键词: 催化氧化; 过氧化氢合成; 反应机理; 反应耦合

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*通讯联系人. 电子信箱: hkung@northwestern.edu

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