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[Review]

A Review on Research Progress in Direct Synthesis of Hydrogen Peroxide from Hydrogen and Oxygen：Noble-Metal Catalytic Method, Fuel-Cell Method and Plasma Method

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Abstract Hydrogen peroxide (H_2O_2) as a high efficient and green oxidant has become one of the 100 most important chemicals in the world. Some current research progresses in the direct synthesis of H_2O_2 from H_2 and O_2 by noble-metal catalyst, fuel cell and plasma have been reviewed systematically in this paper. Perspectives about the development direction and application prospect of the above mentioned three methods have also been discussed.

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1 Introduction

Hydrogen Peroxide (H_2O_2) is a high efficient and green oxidant because of the highest content of active oxygen (47.1 w/w%) and only H_2O by-product [1,2]. H_2O_2 has been listed as one of the 100 most important chemicals in the world [3]. Based on the purity and concentration, hydrogen peroxide is divided into commercial H_2O_2, high purity H_2O_2 and concentrated H_2O_2. Commercial H_2O_2 is classified according to its mass concentration, i.e. 30%, 35%, 50%, 60% and 70%. These commercial H_2O_2 products have been mainly used in bleaching of textile and pulp, treatment of waste water, metallurgy, removal of organic pollutants, production of hydroquinone, etc [4-6]. In recent years, commercial H_2O_2 has also been widely applied in the field of chemical synthesis, such as epoxidation of propylene to produce propylene oxide and oxidation of cyclohexanone amine to produce cyclohexanone oxime [7-11]. In addition, based on the literatures, the commercial H_2O_2 also has potential application in desulfurization of gasoline and diesel [12-14]. High purity H_2O_2, i.e. electronic grade H_2O_2, is mainly used as a cleaning agent, corrosion inhibitor and photoresist removal agent of semiconductor crystal plate in electronic industry, which includes microelectronics, display and photovoltaic technologies. The high purity H_2O_2 has strict requirements and standards regarding the contents of carbon oxides, anions and metal cations, which must confirm to the standards of the Semiconductor Equipment and Materials International Association (SEMI standards) [15]. With the rapid development of electronic industry and information technology, the demand for high purity H_2O_2 will increase continuously [16]. Concentrated H_2O_2 is also called propellant grade H_2O_2. It not only requires electronic grade purity, but also requires mass concentration to be more than 90%, and even 98% [17]. Concentrated H_2O_2 is mainly used as chemical propellant of rockets and torpedos in the fields of military and aerospace. In short, H_2O_2 has important significance on protection and treatment of environment, green synthesis of chemicals, developments of electronics and information industry and improvements of aerospace and military industry.

In 1818, Thenard synthesized H_2O_2 by reaction of barium oxide with nitric acid for the first time. After nearly 200 years, H_2O_2 has become a bulk chemical. As shown in Figure 1, the total annual production capacity of H_2O_2 in 2010 is about 3 million tons [18], which is mainly manufactured by companies of Solvay (Belgian), Evonik (German), Arkema (French) and FMC (American, the business of H_2O_2 production has been taken over by PeroxyChem). However, the forecast demand of H_2O_2 has

been predicted to be more than 4.3 million tons in 2015 [19]. Industrial technologies for production of H_2O_2 has experienced electrolysis, isopropanol oxidation and auto-oxidation (AO) methods, and currently more than 95% of H_2O_2 quantity are produced by the AO process.
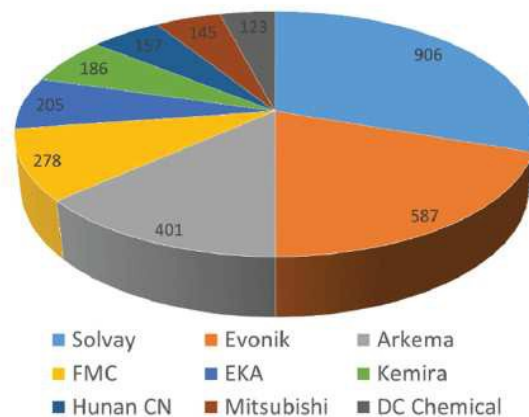
Figure 1   global market distribution of H_2O_2 in 2010（Unit kt/year） [18]
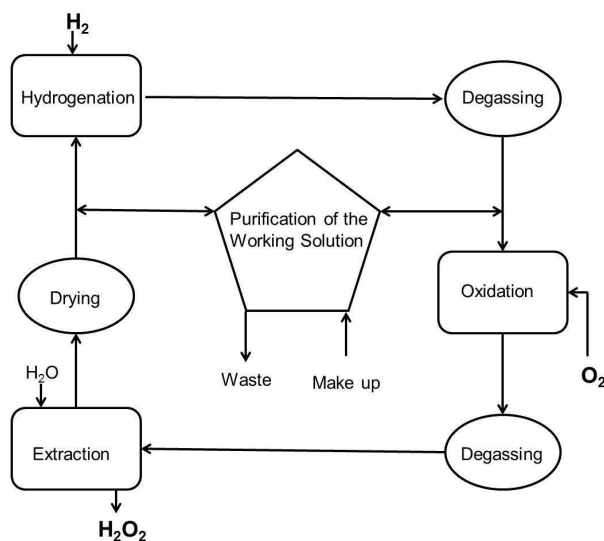
Figure 2   Diagram of the anthraquinone process to synthesize H_2O_2 (Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim) [1]

The AO process was applied in industry by IG Farbenindustrie Corporation (German) in 1940s. This process mainly includes four sections: hydrogenation of anthraquinone (AQ), oxidation of hydrogenized anthraquinone (HAQ), extraction of H_2O_2 and purification and circulation of working solution [1], as shown in Figure 2. Hydrogenation of AQ (2-ethyl-anthraquinone or 2-amyl

anthraquinone) to HAQ takes place in an organic solvent by using Ni or Pd catalysts [20, 21], but Ni catalysts have now been mostly replaced by Pd ones, because the Ni traces in the production are not suitable for home products (allergy). Oxidation of HAQ is an automatic process, which takes place in the absence of catalysts, and the oxidant is air or oxygen-enriched gas. At the same time of generating H_2O_2, HAQ is oxidized to AQ, which is recycled. H_2O_2 produced by the oxidation of HAQ exists in the working solution, which contains aromatic organic compounds, tri-octyl phosphate and tert-butyl urea. After the section of H_2O_2 extraction by solvent, crude H_2O_2 can be obtained. Through further purification and concentration operations (distillation), the commercial H_2O_2 products with different concentrations (30%, 35%, 50%, 60% and 70%) are available. At last, the working solution is purified by activated alumina (remove some wastes), and then is recycled to be used (need make up some new working solution). The purpose of the purification and circulation of working solution section is to recycle AQ.

High purity H_2O_2 and concentrated H_2O_2 is produced from the above mentioned commercial H_2O_2 by using some deep purification and concentration operations. Commercial H_2O_2 solution contains a small quantity of mechanical impurities, inorganic impurities and organic impurities. The organic impurities include some degradation products and by-products, i.e. ester, phenols, alcohols and ketones. Purification methods of H_2O_2 include [22]: distillation, ion exchange resins, membrane separation, supercritical fluid extraction and crystallization. In order to obtain high purity H_2O_2 products, generally, we need to use a variety of purification methods, which consume huge energy. In recent years Abejon et al. [23-25] used multi-step reverse osmosis purification process to purify commercial H_2O_2, and the product is high purity H_2O_2 solution, which meets the standards of SEMI. However, this process needs to be simplified and the life of the membrane material also needs to be improved. Concentrated H_2O_2 is generally produced from high purity H_2O_2 by using vacuum distillation and recrystallization operations, which consume huger energy.

The advantage of AO process is that, by using the hydrogenation reaction of AQ and oxidation reaction of HAQ, H_2 and O_2 can react with each other to generate H_2O_2 without direct contact. Therefore, the AO process is safe and, it is suitable for large-scale and continuous operation. The main disadvantages of AO process is that, firstly, this process can be only operated at large-scale, thus some security risks in the processes of transportation and storage must be undertaken by the users; secondly,

the AO process have problems of emitting exhaust gas (mesitylene isomers), waste water (containing aromatics, 2-ethyl-anthraquinone, tri-octyl phosphate, tert-butyl urea and K_2CO_3 lye) and solid waste (activated alumina).

2   Technologies for Direct Synthesis of H_2O_2 from H_2 and O_2

Because of the above mentioned problems of AO process, researchers proposed the direct synthesis of hydrogen peroxide (DSHP) from H_2 and O_2, which is a typical green and atomic economic chemical reaction. Currently, this direct synthetic route is mainly achieved by the principles of noble metal catalysis, fuel cell and plasma.

2.1 H_2/O_2 Noble Metal Catalytic Method

In 1914, Henkel et al. [26] firstly proposed the DSHP from H_2 and O_2 by noble metal catalysis. In recent years, it has become a research focus in the field of noble metal heterogeneous catalysis. Typical reaction conditions are as follows: H_2/O_2 mixture feed gas (oxygen excess, hydrogen concentration is less than 4 mol%), supported noble metal catalysts, acidic methanol solvent, nearly 0 □ reaction temperature, atmospheric or positive pressure and gas-liquid-solid three phases reaction.

The noble metal catalytic method improves the security of the H_2/O_2 reaction to synthesize H_2O_2 mainly by adding an inert gas, using solvents and limiting hydrogen feed ratio ($H_2 < 4$ %). However, solvents and limited hydrogen feed ratio will both reduce the efficiency of synthesizing H_2O_2. To resolve this conflict, researches used supercritical CO_2 solvent and membrane catalysts. Noble metal catalyzing H_2/O_2 reaction is complicate, and it contain three side reactions, i.e. combustion of hydrogen ($H_2 + 1/2O_2 \rightarrow H_2O$), hydrogenation of H_2O_2 ($H_2O_2 + H_2 \rightarrow 2H_2O$) and decomposition of H_2O_2 ($H_2O_2 \rightarrow H_2O + 1/2O_2$), which result in the formation of H_2O by-product (Figure 3). In order to improve the selectivity and productivity of H_2O_2, researches have been focused on the active components, supports and preparation methods of catalysts, as well as side reaction inhibitors, solvent, pressure and temperature.
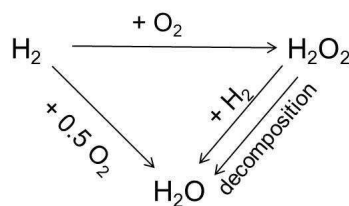

Figure 3   Diagram of the reaction network of noble metal catalytic H_2/O_2 reaction

2.1.1 The reaction mechanism of noble metal catalytic method

Kobozev et al. [27]proposed the reaction mechanism of the DSHP from H_2 and O_2 over a Pd catalyst: firstly, hydrogen molecules dissociate into hydrogen atoms on the surface of the Pd catalyst, then, oxygen molecules adsorb and react with hydrogen atoms to form HO_2 adsorbed intermediate species, at last, HO_2 species react with hydrogen atoms to form H_2O_2 molecules on the surface of the Pd catalyst. Lunsford et al. [28] have done an isotope tracer experiment (using $^{18}O_2/^6O_2 = 1/1$ as oxygen feed), in which it has been found that $H_2^{18}O^{16}O$ specie was not present in the H_2O_2 product. Therefore, it can be evolved that the main reaction path of forming H_2O_2 is the reaction between oxygen molecules and hydrogen atoms (Figure 4) [29]. Staykov and Todorovic supported the above reaction mechanism by using theoretical calculations [30, 31]. These mechanism studies provide an useful guide for the design and preparation of catalysts [32]: the stronger the ability of the catalyst to dissociate H_2 is, the faster the H_2O_2 may generate; the weaker the ability of the catalyst to dissociate O_2 is, the higher the selectivity of H_2O_2 may be.
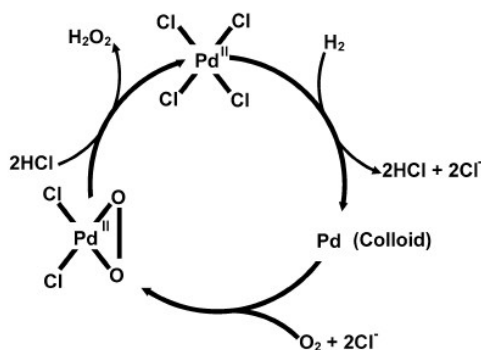
Figure 4 Diagram of the reaction mechanism of DSHP on Pd catalyst (Copyright © 2004 Elsevier Inc.) [29]

2.1.2 Active components of noble metal catalyst

The active component of the catalyst is the key point for the DSHP. Supported Pd, Au, Pt, Pd-Au, Pd-Pt, Ru-Au, Ru-Pd and Pt-Au-Pd catalysts have been reported.

Lunsford and Hutchings et al. took the lead to study the performance of the supported Pd [33-36] and Au [37-39] catalysts in the DSHP. In the patent of Headwaters [40], Zhou et al. firstly proposed that crystal structure (FCC, HCP, BCC, etc) and crystal plane (111, 110, 100, etc) of metal particles could have significant influence on the direct synthesis of H_2O_2. Kim et al. [41, 42] studied the effect of the

crystal plane and the particle size of Pd catalysts on H_2O_2 synthesis, and found that the larger particle size and (111) crystal plane are favorable for this reaction. Iwamoto et al. [43], using density function theory (DFT) calculation, found that the unsaturated activity sites (with fewer coordination number) located on the crystal angles and crystal edges of Pd particles are easy to result in the formation of H_2O by-product, however, the saturated activity sites (with more coordination number) located on the (111) crystal plane of Pd particles are beneficial to generate H_2O_2. Han et al. [44] compared the catalytic performance of (111), (100) and (110) crystal planes of Pd particles in H_2O_2 synthesis by DFT calculation, and found that Pd (111) crystal plane benefits the synthesis of H_2O_2 mostly. Meyer et al. [31], also using DFT calculation, studied the reason for generation of H_2O by-products on the surface of Pd, Pt and Au single metal catalysts. Results showed that the generation of H_2O is caused by the dissociation of O_2, the dissociation of OOH intermediate species and the decomposition of H_2O_2 on Pd, Pt and Au catalysts, respectively. That is, catalysts based solely on Pd, although active for the synthesis of hydrogen peroxide, are also active in O-O scission leading to H_2O formation.

On the basis of the above mentioned single metal catalysts, people then studied the performance of Au-Pd [45-58], Pd-Pt [59,60], Ru-Au and Ru-Pd [61] bimetallic alloy catalysts in the DSHP. In general, bimetallic alloy catalysts have a higher selectivity in H_2O_2 than that of single metal catalysts. Hutchings et al. [55], by using colloid preparation and subsequent colloid immobilization steps, prepared AuPd bimetallic particles on both activated carbon and TiO_2 supports with Pd{Au} (Pd-shell/Au-core) and Au{Pd} (Au-shell/Pd-core) morphologies, which were observed by using STEM-HAADF and STEM-XEDS technologies. It has been found that, compared with the normal AuPd catalysts created by simultaneous addition and reduction of both metal precursors (Au and Pd are randomly alloyed), both the Pd{Au} and Au{Pd} core-shell catalysts showed lower catalytic activity for the synthesis of H_2O_2, which could be caused by high rate of H_2O_2 hydrogenation reaction. Ishihara et al. [56] prepared Au-Pd bimetallic catalysts with different Au compositions and, they found out that the H_2O_2 formation rate increased with increasing concentration of Au, but the decomposition rate of H_2O_2 in the presence of colloidal Pd-Au decreased with increasing Au content. Further DFT calculation results [57, 58] indicate that the competitions between the dissociation of H_2O_2 and the release of H_2O_2 on the catalyst surface determines the reaction selectivity. Au atoms on the surface of Au-Pd alloy can weaken the interaction of the metal surface with H_2O_2, and thus facilitate the release of H_2O_2 and suppress the

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decomposition of H_2O_2 [57, 58]. Through experiments, Han et al. [62] found that, in the Au-Pd alloy catalyst, Pd atom surrounded by Au atoms is the best active site to synthesize H_2O_2, as shown in Figure 5. Through DFT calculations, Staykov et al. [30] found that Au atoms on the Au-Pd bimetallic catalyst surface can prevent oxygen dissociation, thereby increasing the H_2O_2 selectivity. Ham et al. [63] have also got a similar conclusion as Staykov. Han et al. [64], through the comparative study of Pd, Au and Pd-Au alloy catalysts, found that electron transfer exists between Au and Pd in Pd-Au alloy catalyst. The function of Au in regulating the electronic structure of Pd may be one of the important reasons why Au-Pd alloy catalysts have higher selectivity for H_2O_2 synthesis. Under the situation of Pd-Pt alloy catalysts, electron transfer also took place between Pt and Pd [59,60]. Introducing a small amount of Pt into the Pd catalyst may result in electron transfer from Pd to Pt, which can reduce the strength of Pd-O bond, thereby inhibiting the dissociation of O_2 and enhancing the selectivity of H_2O_2. However, when excessive amount of Pt (Pd/Pt<8) is introduced, Pt gathers on the surface of the alloy catalyst, which having adverse effect on the adsorption of reactant molecules and the stability of OOH (reaction intermediate) and H_2O_2.
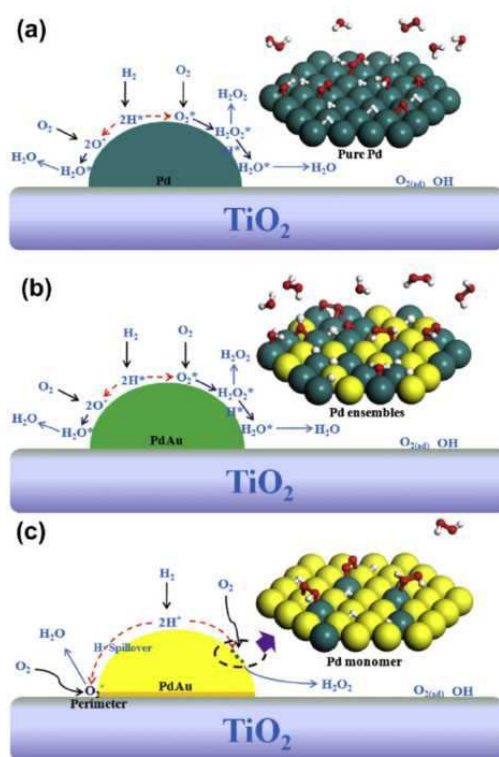

Figure 5   Schematic diagram of reaction mechanism for direct synthesis of H_2O_2 on (a)Pure Pd、(b)Pd ensembles and (c)Pd monomer catalyst (Copyright © 2013 Elsevier Inc.) [62]
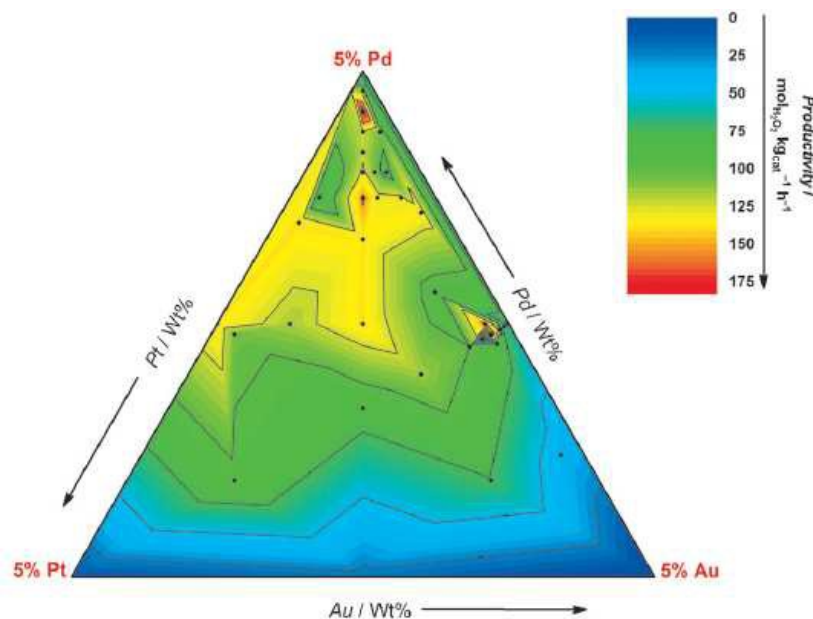
Figure 6   Rate of H_2O_2 synthesis from 5 wt% Pt-Au-Pd three metal catalysts with different compositions (Copyright

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Table 1. Some latest results of H_2O_2 synthesis from H_2 and O_2 on noble-metal catalysts

Catalysts	H_2O_2 selectivity	H_2O_2 formation rate	Concentration of H_2O_2	Reference/Year of publication
5% Pd@TiO$_2$	70%	132 $g_{H2O2}\ g_{Pd}^{-1}h^{-1}$	—	[66]/2013
Au-Pd@TiO$_2$	67%	3.78 $mmolh^{-1}$	1.8 %	[67]/2013
0.4Au-1.1Pd@Ti-NT	—	174.9 $mmol_{H2O2}\ g_{cat}^{-1}\ h^{-1}$	0.14%	[68]/2014
Pd@XC-72	74%	129 $mmolg^{-1}h^{-1}$	1.67%	[69]/2014
0.2Pt-0.2Au-4.6Pd	—	184 $mmol_{H2O2}\ g_{cat}^{-1}\ h^{-1}$	—	[50]/2014
1.0Au-2.0Pd	48%	2330 $mmol_{H2O2}g_{metal}^{-1}h^{-1}$	—	[62]/2014
Au@hollowSiO$_2$	15%	1125 $mmol_{H2O2}\ g_{cat}^{-1}\ h^{-1}$	—	[39]/2015
2.5Au-2.5Pd	—	252 $mmol_{H2O2}\ g_{cat}^{-1}\ h^{-1}$	0.5%	[52]/2015
Au-Pd@SZ	55%	13.6 $mmolg^{-1}h^{-1}$	—	[53]/2015
1Au-3Pd	56%	1141 $mmol_{H2O2}\ g_{cat}^{-1}\ h^{-1}$	0.12%	[54]/2015
Au-Pd	60%	17.5 $mmol_{H2O2}h^{-1}$	5.8%	[70]/2015
Au-Pd	99%	32 $mmol_{H2O2}h^{-1}$	0.12%	[71]/2015

Recently, Hutchings et al. [50, 65] studied the Pt-Au-Pd trimetallic catalysts, and found that introducing a small amount of Pt into Au-Pd bimetallic alloy can suppress the hydrogenation and decomposition of H_2O_2, which thereby increased the yield of H_2O_2, as shown in Figure 6. From this, it can be seen that alloying is a important path to improve the performance of noble metal catalysts in H_2O_2 synthesis. Some latest experimental results about H_2O_2 synthesis on noble metal catalysts are shown in Table 1. It can be seen that the concentration of H_2O_2 is still very low, and the selectivity and formation rates of H_2O_2 are heavily dependent on the concentration. The reason is that, in the case of higher concentration, the side reactions (hydrogenation and decomposition) would be aggravated and, the catalysts would be less stable.

2.1.3 Supports of noble metal catalysts

Property of supports is another key factor which affects catalytic performance of supported catalysts. In the DSHP, reported support materials include zeolites [38, 72-75], metal oxide [46, 67, 68, 76-80], carbon materials [69,71,81-83], silica [84-89], resin [90-92], heteropoly acid [93-97] and membrane materials [98-107], etc.

Acidity is an important nature when zeolites, metallic oxide, silica, resin and heteropoly acid materials act as supports. Some scholars' researches have shown that increase of acidity can promote the DSHP [75,78,93-97]. In fact, some inorganic acids are commonly used in reaction solvent, thus it is easy to understand that acidity of supports is beneficial to the synthesis of H_2O_2. Park and Fierro et al. [84-87] studied the performance of Pd catalyst supported on SO_3H functional silica in the DSHP, and found that SO_3H functional processing can not only promote the generation of H_2O_2, but also make the synthesis process to be operated using less inorganic acid, which to some extent reduce the corrosion of reactor and the loss of active metal. It is reported that Lee and coworkers [90-92] made the DSHP to be operated continuously by using SO_3H functional resin as catalyst support, concentration of H_2O_2 solution reached 9.9 wt %. Recently, Edwards et al. reviewed the use of acidic supports systematically, and pointed out that the isoelectric point of the support was a key factor in the stabilization of H_2O_2 under reaction conditions. That is, supports with low isoelectric points such as carbon materials are beneficial for the stabilization of H_2O_2 [108].

The presence of dopants (chemical groups or ions) on the support have significant effects on the

DSHP. Abate et al. [81-83] studied the Pd and Au-Pd catalysts supported on carbon nanotubes and, found that N doping carbon nanotubes support is favorable to the dispersion and stability of Pd nanoparticles. Therefore, generation rate of H_2O_2 have be improved. In addition, it was postulated that the introduction of N functional groups would also increase the acidity of the catalyst surface, which will increase the stability of H_2O_2. Strukul et al. [109] investigated the catalytic performance of Pd catalysts supported on SO_4^{2-}, Cl^-, F^-, and Br^- doped zirconia in H_2O_2 synthesis under mild conditions (20℃, 1 bar) and, found that using a doped support could generally improve the production rate and selectivity towards H_2O_2, especially in methanol solvent. By using kinetic analysis, they further found out that the H_2O_2 hydrogenation constants were about the same for the SO_4^{2-}, F^-, and Br^- doped samples and the nondoped samples, which means that the hydrogenation rate is affected more by acidity and to a lesser extent by the doping anions, in agreement with the observation of Lunsford et al [29]. However, Cl^- doping will accelerate the reaction rates toward H_2O generation (direct generation of H_2O and hydrogenation of H_2O_2) more than that toward H_2O_2 synthesis. It is also worth noting that, the doping content should be carefully investigated, because excess doping element might be leached into the reaction medium and readsorbed on the surface of metal particles, even poisoning the catalyst. Hutchings et al.[52], by using insoluble heteropolyacids support and water solvent, studied the effect of metal ions (Cs^+, Rb^+, K^+ and Ag^+) and, found that the catalysts containing Cs^+ and Rb^+ were shown to be extremely active for H_2O_2 synthesis. Gudarzi et al. studied the factors affecting catalytic decomposition of H_2O_2, and found out that the presence of oxygen-containing surface functional groups on the carbon supports can stabilize H_2O_2 in the solution and reduce its decomposition and hydrogenation [110]. Nevertheless, carbon materials have another problem, that is the surface COOH functional group is unfavorable to H_2O_2 synthesis. The reason is that COOH functional groups can increase hydrophilicity of the catalyst surface, which will trigger the decomposition of H_2O_2 on the surface of the catalyst.

The textural properties of supports have also been investigated. Hu et al. [69] found that, compared with some other carbon supports, the graphitized carbon support can improve the selectivity of H_2O_2, and the authors attributed high H_2O_2 selectivity to the high structure order degree of graphitized carbon support. Strukul et al. studied the effect of the textural properties (pore size distribution and wall thickness) of the mesoporous silica supports (MCM-41 and SBA-15) on the

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activity and selectivity of Pd-based catalysts [88], in which a close correlation between the textural properties of the support and the catalytic activity of the examined samples has been found. As shown in Figure 7, in the case of MCM-41, the samples show high activity but poor selectivity as well as poor stability. Because of narrow pores (2.9 nm), some small Pd nanoparticles (about 2 nm in the channels) and a fraction of large Pd particles (lying outside the support channels that is small in number but large in weight) were prepared, but the outside Pd particles could hamper the way through the pores. The small Pd nanoparticles is very active due to the presence of more energetic Pd sites (defects, edges and corners) but the selectivity drops down, because these energetic sites will trigger the H_2O generation through dissociative chemisorption of O_2. In addition, the thin wall thickness of the MCM-41 renders it extremely sensitive towards stability problems. However, in the case of SBA-15, the samples show very good catalytic performance in terms of activity and selectivity. Because of sufficiently large pore size of SBA-15, it is beneficial to obtain a catalyst with suitable Pd average diameter (4.5 nm), which could get a right compromise between a high dispersion leading to high activity and the presence of less energetic sites to avoid a drop in selectivity, and where almost 90% of the palladium present is usefully located inside the pores to avoid the formation of catalytically inactive Pd particles. The sufficiently large pore size of the SBA-15 also allow an easy diffusion of reagents and products. Besides, thicker wall thickness of the SBA-15 supported catalysts allows a good mechanical stability and reusability.
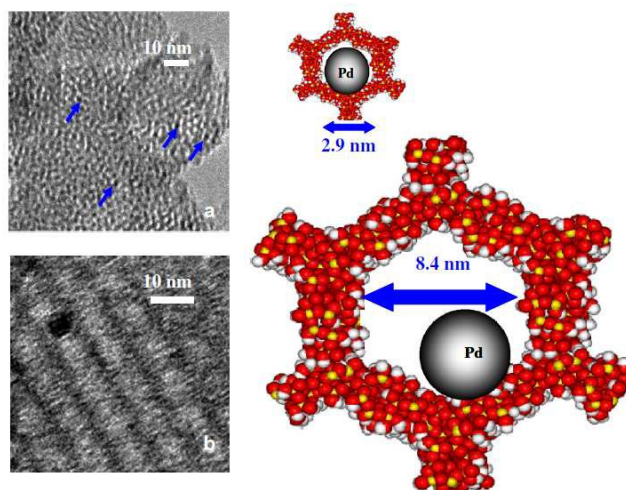

Figure 7. HRTEM image of a Pd particle inside a channel taken along the (110) direction of MCM-41 (section a) and of SBA-15 (section b). On the right, schematic representation of the pores size of the mesoporous systems [88].

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Membrane supports with good permeability can improve the security of the DSHP. The reason is that, by using membrane materials as the support to prepare membrane catalysts, H_2O_2 can be synthesized without direct contact between H_2 and O_2. In this regard, Strukul and coworkers had prepared supported Pd, Pd-Pt and Pd-Ag membrane catalysts using porous alumina film, porous alumina tube or porous ceramic tube as the support [98-100]. In the process of membrane catalysis, H_2 dissociate over metal active sites into hydrogen atoms, which can penetrate the membrane catalyst and react with O_2 on the other side of the membrane catalysts to form H_2O_2. At present, the main problems of membrane catalysts is the low reaction efficiency caused by low rate of mass transfer. The performance of membrane catalysts in H_2O_2 synthesis can be improved by surface decoration and modification [101-107]. However, these relevant researches are challenging.

2.1.4 Preparation method of catalyst

In addition to the metal active component and support, the performance of the catalyst is also closely related to the preparation methods. There have been a lot of researches [72,76,111-114] about preparation methods of catalysts in the DSHP. Mori et al. [72,111] reported that the activity of Pd-Au/Ti-MCM-41 and nanoscale Pd/CsHPA/SiO$_2$ (CsHPA: cesium salt heteropoly acid) catalysts prepared by high pressure mercury lamp light deposition was much better than that prepared by ordinary deposition method. The authors thought that, under the condition of illumination, optical excitation sites of the support materials can interact with metal precursor to form smaller metal nanoparticles. Hutchings et al. [76,112] investigated the preparation methods and loading sequence of bimetallic catalysts, and found that the Pd-Au/ZrO$_2$ catalyst, prepared firstly by Au deposition precipitation and secondly by Pd incipient-wetness impregnation, has higher Pd content and better performance of H_2O_2 synthesis. Lee et al. [114], through encapsulating Pd nanoparticles into SiO$_2$ hollow ball by the Stober method, prepared the core-shell structure Pd@SiO$_2$ catalyst, which has higher Pd dispersion and more uniform Pd particle size compared with normal supported Pd/SiO$_2$ catalyst. Therefore, yield of H_2O_2 and stability of catalyst is improved sharply. Sterchele et al. [115] investigated the effect of the metal precursor-reduction by using different reducing agent on Pd-Au and Pd-Pt catalysts, and found that formaldehyde, compared with H_2, as the reducing agent can improve the activity and selectivity of Pd-Au and Pd-Pt catalysts.

Furthermore, acid treatment and heat treatment on carbon supports can significantly improve the

reaction performance of carbon supported catalysts [71,116-119]. Hutchings et al. [116,117] found that, using carbon materials pretreated by acid as the support, highly dispersed Au-Pd bimetallic catalysts could be prepared and then high selectivity of H_2O_2 could be got. Solsona et al. [71] also found that, using orderly mesoporous carbon pretreated by acid as support, the size of the Au-Pd alloy could be reduced to be about 2 nm and the selectivity of H_2O_2 reached 99%. Moreover, Hutchings et al. [118,119] found that heat treatment (post-process) can improve the metal particle morphology and dispersion of carbon supported catalyst (Au-Pd), thus the stability and recycling performance of the catalyst can be improved.

2.1.5   Side-reaction inhibitor

Inorganic acids and halides are commonly used as side-reaction inhibitors in the DSHP. H_2O_2 belongs to weak acid, therefore, inorganic acid can, to some extent, stable H_2O_2 molecule, inhibit the decomposition of H_2O_2 and improve the selectivity of H_2O_2 [120,121]. Same as doping halides on the support [56], addition of halides to the reaction medium can also achieve the goal of improving H_2O_2 selectivity. The role of the halides, on one hand, is to inhibit hydrogenation of H_2O_2 by changing the catalyst surface charge; on the other hand, is to inhibit the side-reaction of generating H_2O by poisoning the active sites on which dissociation of oxygen takes place. Choudhary et al. [77,122-128], after a number of studies, found that bromide is the best side-reaction inhibitor for H_2O_2 synthesis, and found that the side-reaction inhibiting effect would be better if two kinds of halides were added simultaneously. For example, when bromide and fluoride or bromide and iodide were added in the reaction system, the three reaction relating with H_2O formation (combustion reaction of hydrogen, decomposition reaction of H_2O_2 and hydrogenation reaction of H_2O_2) can all be suppressed, therefore, selectivity of H_2O_2 can be improved significantly. Using DFT calculation, Iwamoto et al. [43] found that Br^- ion coming from bromide inhibitor could coordinate with Pd atoms located on the crystal angles and crystal edges of Pd particles by competitive adsorption, so as to suppress the side reactions (see Figure 8). Kim et al. [129], using high resolution transmission electron microscopy (HRTEM), observed that halogen ions could cover the (100) crystal plane of Pd nanoparticles, so as to inhibit O_2 dissociation and improve H_2O_2 selectivity. Centomo et al. [130] characterized the catalyst using extended X ray adsorption fine structure (EXAFS) during the reaction, and found that Br^- ion can inhibit the oxidation of Pd nanoparticles, so that the Pd maintain metallic state and H_2O_2 decomposition

can be avoided. In addition to inorganic acids and halides, oxidized state of Pd (PdO) has also been found to make the catalysts less active in H_2O_2 decomposition [110].
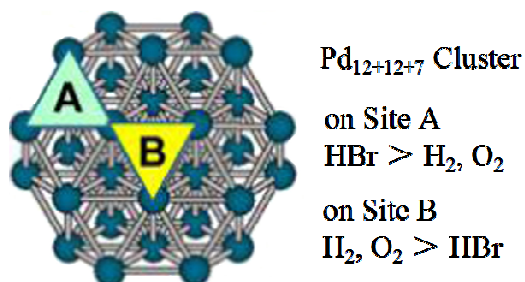

Pd$_{12+12+7}$ Cluster

on Site A
HBr $>$ H$_2$, O$_2$

on Site B
H$_2$, O$_2$ $>$ HBr

Figure 8   Mechanism schematic diagram of side-reaction inhibition of HBr [43]

Site A：Pd atoms located on the crystal angels and crystal edges；Site B：Pd atoms located on 111 crystal plane.

(Copyright © 2013, American Chemical Society)

Although inorganic acids can effectively improve the selectivity of H_2O_2, they can also dissolve and etch the active component of the catalyst. In the catalytic system for the DSHP, how to avoid the dissolution loss of noble metal catalyst is a challenging problem. Ishihara et al. [70] found that adding bromide and phosphoric acid in the reaction system can significantly reduce the dosage of bromide and inorganic acid, which, to a certain extent, reduced the loss of catalyst. Hutchings et al. [131,132] found that impregnation modification (using NaBr solution) on the prepared Au-Pd catalyst can reduce the dissolution loss of the active component. However, this method has to deal with the leaching of bromide from the catalyst and, the long term running performance should be investigated.

2.1.6   Solvent

The H_2/O_2 reaction for the DSHP catalyzed by noble metal catalysts usually takes place in organic solvent. The main function of the solvent in the DSHP is to reduce the resistance of mass transfer by dissolving H_2 and O_2, so as to improve the reaction efficiency. Currently, the DSHP is mostly carried out in methanol because of high solubility of H_2 and O_2. The patent of Enichem [133] reported that the DSHP in methanol solvent can be integrated with propylene oxidation to propylene oxide (PO) catalyzed by TS-1. Even so, the use of methanol solvent will bring a huge volume of flammable solvent to the reaction medium, therefore, the cost of the separation, usually by distillation, will be huge. To address this issue, some scholars have tried water instead of methanol solvent [134,135]. However,

under the condition of H_2O solvent, there are some other problems, such as low rate of reaction due to low solubility of feed gas and bad stability of catalyst. Furthermore, supercritical carbon dioxide (CO_2) have also been reported as a good solvent in the DSHP (Figure 9). For example, Beckman et al. [136-141], under the condition of supercritical CO_2 solvent and supported Pd catalyst, got 31.7% H_2O_2 yield and 56.1% H_2O_2 selectivity; Pashkova et al. [66,142], in a similar catalytic system, got 70% H_2O_2 selectivity and 132 $g_{H2O2}g^{-1}_{Pd}h^{-1}$ H_2O_2 space-time yield. The advantages of supercritical CO_2 solvent are that of high solubility of H_2 and O_2 and easy separation of H_2O_2. However, selectivity of H_2O_2 need to be improved in the future.
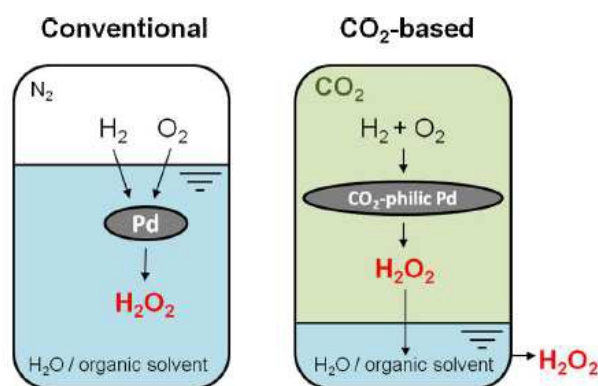

Figure 9   Diagram of reaction process for the DSHP in supercritical CO_2 solvent (Copyright © 2014 Elsevier B.V.)

[142]

2.1.7   Pressure

The DSHP from H_2 and O_2 is a complex gas-liquid-solid three-phase reaction process, and mass transfer resistance will usually limit the reaction rate. Therefore, the reaction pressure is a key factor because it is directly related to the mass transfer of the reactant gases to the liquid phase. Generally, total pressure of the system increases the solubility and decreases bubble size of feed gas, which will increase the mass transfer efficiency. That is, the higher the pressure of H_2 and O_2 in the gas phase the higher the concentration of of H_2 and O_2 in the liquid phase and, therefore the higher their concentration in the vicinity of the catalyst sites, which will enhance the reaction rate. Moreno et al. [143], by using a nano-Pd/C commercial catalyst, methanol solvent and a semi-continuous reactor, studied the influence of pressure (0.1~0.9 MPa) on the DSHP. The reaction results indicate that the

production of H_2O_2 increases linearly with increasing pressure due to an enhanced solubility of the reactant gases. Hutchings et al. [47] studied the influence of pressure (0.5~1.3 MPa) in a continuous microreactor and, found that as the system pressure increased, the H_2 conversion increased while the selectivity of H_2O_2 remained constant. These results show that pressure had no effect on H_2O_2 selectivity, indicating that the rate of synthesis and degradation (hydrogenation and decomposition) increase proportionately because both reactions are related to the hydrogen partial pressure. Voloshin et al. [144] also investigated the system pressure using a microreactor, but their experimental data show that the selectivity increases with increasing pressure while conversion decreases up to a pressure of 1.4 MPa, where both conversion and selectivity remain constant on further increasing the pressure. For the future industrial application, appropriate pressure should be investigated to find a compromise between expensive equipment and time-space yield of H_2O_2.

2.1.8   Temperature

Reaction temperature is another important parameter that affects reaction rate by changing the reaction rate constant and solubility of the reactant gases in the used solvent. Hutchings et al. [47] investigated the effect of reaction temperature on H_2O_2 synthesis at constant gas and liquid flow rates, and found that increasing the reaction temperature resulted a decrease in the H_2O_2 concentration produced during the reaction. The experimental results show that as temperature increases, the conversion of H_2 increases from 20% at 2℃ to 30% at 30℃ while the selectivity toward H_2O_2 decreases. The effect could be due to the different activation energies of the synthesis reaction and subsequent degradation reactions (hydrogenation and decomposition), as well as different solubility of the H_2 and O_2 in the solvent at the specific temperatures [2,145]. Biasi et al. studied the effect of temperature (-5, 0, 10 and 40℃) on the conversion of H_2 and production of H_2O_2, by using a batch reactor and methanol solvent [146,147]. Experimental results show that although the conversion increases with temperature, the concentration of H_2O_2 reaches a maximum at -5℃ and a minimum at 40℃, that is, the selectivity of H_2O_2 decreases with temperature. Through kinetic analysis, they found that the activation energy of H_2O_2 synthesis (about 24 kJ mol^{-1}) is lower than that of hydrogenation and decomposition (about 45 kJ mol^{-1}), which could be the reason why a higher selectivity is achievable at low temperature. Serna et al. [148] studied the kinetic temperature dependence in a semi-continuous reactor at both low catalyst amounts (15 mg, corresponding to a kinetic regime) and higher catalyst

amounts (100 mg, corresponding to a mass transfer). It has been found that the productivity of H_2O_2 decreases with temperature in the case of low catalyst amounts, while increases with temperature in the case of higher catalyst amounts. Pashkova et al., using 5% Pd-TiO$_2$ catalyst and variety H_2/O_2 ratio, studied the effect of temperature (27 and 40℃) at low conversion [66]. Where, an increase in productivity and conversion with temperature independently on the H_2/O_2 ratio has been found. All in all, low temperature is favorable to get a higher selectivity, while relative high temperature is beneficial to get a higher conversion and productivity. The real operation temperature in a industrial plant should comprehensively consider the factors of heat transfer efficiency, reaction selectivity, utility cost and safety issue.

2.1.9 Engineering problem

In 2003, the patent of Enichem [133] ever proposed a new route for the production of PO, which is realized through the combination of the DSHP catalyzed by Pd catalyst and propylene oxidation catalyzed by TS-1 zeolite catalyst, in an alcohol or mixture of alcohols, MTBE and water [149, 150]. The patent of International Business Machines Corporation described a multi-step process for the production of concentrated H_2O_2 aqueous solutions (15~60 wt%) through the DSHP [151]. It is worth noting that Headwaters Technology Innovation (HTI) ever produced a robust catalyst technology that enables the DSHP in industrial scale [152]. This breakthrough technology, called NxCatTM, is a Pd-Pt catalyst supported on spherical Al$_2$O$_3$ (Figure 10), although their patents ever reported some efficient Pd catalysts supported on carbon materials [40, 153]. The NxCatTM catalysts is efficient because of their precisely controlled surface morphology [152]. This catalyst has a uniform 4-nanometer feature size that safely enables a high rate of production with a hydrogen gas concentration below 4 percent in air (i.e., below the flammability limit of hydrogen). It also maximizes the selectivity for H_2O_2 up to 100 %. In 2005, HTI cooperated with the Degussa (Degussa-Headwaters) and, made a pilot plant test for the DSHP [154]. In addition, they combined DSHP with propylene epoxidation process, and developed a technology for production of PO by adopting the Degussa-Uhde technology. The above mentioned coupling process can reduce the cost of PO production about 1/3, and even 1/2. Because of the above mentioned achievements, HTI was honored with Presidential Green Chemistry Challenge Winners (2007 Greener Reaction Conditions Award) [152]. However, so far, there were no new reports about industrialization of DSHP.
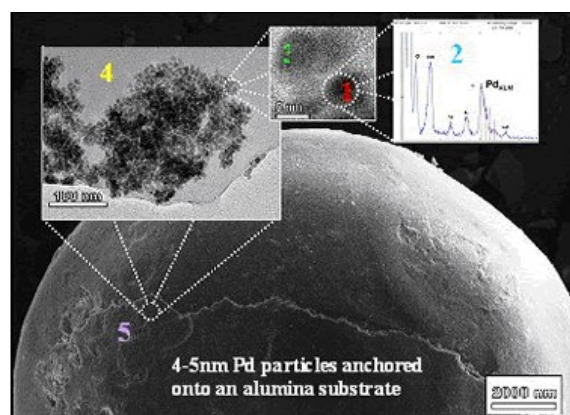
Figure 10. TEM and SEM of the nano-Pd-Pt catalyst developed by HTI company (Website of HTI) [152]

The above mentioned patents and pre-commercial results indicate that H_2/O_2 noble metal catalytic method will most likely replace the AO process to become a large-scale green technology for synthesis of H_2O_2 in the future. However, a crucial problem we must consider is the engineering [155, 156], which could be one of the fatal factors why there is no new industrial result about the DSHP up to now.

The most important engineering problem to be solved is the safety of the operation. The design and selection of the reactor is the core of the engineering problems, because the structure of the reactor determines the safety and reaction effectiveness. At present, the literature mostly adopted laboratory-scale batch or semi-continuous reactor [157], and there are also some reports adopting consecutive trickle bed reactor [158, 159], micro-channel reactor [160], micro reactor [161] and tubular membrane reactor [162]. Recently, Edwards et al. have reviewed the use of flow reactors in the DSHP [108]. Broadly speaking, for the commercial application in the future, the DSHP in a specific reactor must be operated continuously to reduce the contact time with the catalyst, which can minimize the hydrogenation and decomposition rates of H_2O_2. Up to now, the DSHP is only able to produce 10 wt% H_2O_2 solution (optimistic maximum), which could be used directly only under the situation of in site application through integration with some other processes. Otherwise, the low concentration will bring huge transportation costs. Therefore, a concentration process is necessary [151]. In addition, another engineering problem should be considered is how to separate the additives (acid, halides and heavy metals) from the final H_2O_2 product [163].

2.2   Direct synthesis of H_2O_2 through H_2/O_2 fuel cell

The reaction device of the H_2/O_2 fuel cell for H_2O_2 synthesis consists of anode, electrolyte membrane and cathode. The principle of this method to synthesize H_2O_2 is that H_2, under the catalysis of anode catalyst, dissociate into H^+, which pass through the electrolyte membrane to the surface of the cathode catalyst and react with adsorbed O_2 to generate H_2O_2. That is, two electron reduction of O_2 leads to the production of H_2O_2 while four electron reduction results in the formation of H_2O, as shown in the following two reaction equations.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
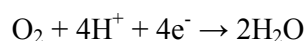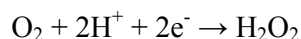
In the 90s, Dow Chemical and Huron Chemical ever jointly developed a trick-bed electrolytic cell for making an alkaline hydrogen peroxide solution, by cathodic reduction of oxygen [164]. By using the cathode consists of graphite chips coated with a mixture of carbon black and Teflon, a solution of 2 wt% hydrogen peroxide in sodium hydroxide was obtained, under the condition of 25 ℃, 2 volts and 0.031 A/cm^2. After that, Yamanaka et al. [165] reported a H_2/O_2 fuel cell method for H_2O_2 synthesis in 1990. Initial fuel cell reaction device (as shown in Figure 11, left) adopted the Nafion-H/Pt as anode, used graphite or gold net as the cathode, and employed hydrochloric acid solution as the electrolyte. This H_2/O_2 fuel cell, under the condition of 5 kPa hydrogen pressure and 101 kPa oxygen pressure, produced H_2O_2 solution with concentration of only 0.2 wt %. The low H_2O_2 concentration were caused by low solubility of O_2 in electrolyte and rapid decomposition of H_2O_2 on the cathode, especially under the condition of low O_2 concentration.

In order to increase the concentration of H_2O_2 solution, Yamanaka et al. [166] then designed a new H_2/O_2 fuel cell device (as shown in Figure 11, right). In this new device, porous carbon composite electrode, made of carbon fibre and PTFE through hot-pressing, was adopted as both the cathode and the anode materials, and NaOH alkaline solution was adopted as electrolyte. The device overcame the problem of low O_2 solubility in the electrolyte and significantly increased the oxygen pressure on the porous cathode(101 kPa), which not only accelerated the reduction reaction of O_2 to generate H_2O_2, but also inhibited the excessive reduction reaction of H_2O_2 to form H_2O by-product. Therefore, selectivity of H_2O_2 reached 93% and concentration of H_2O_2 solution came to 7 wt %. Based on this work, Yamanaka et al. [167-173] investigated the influence of cathode materials and electrolyte on the performance of H_2/O_2 fuel cell, as shown in Table 2.
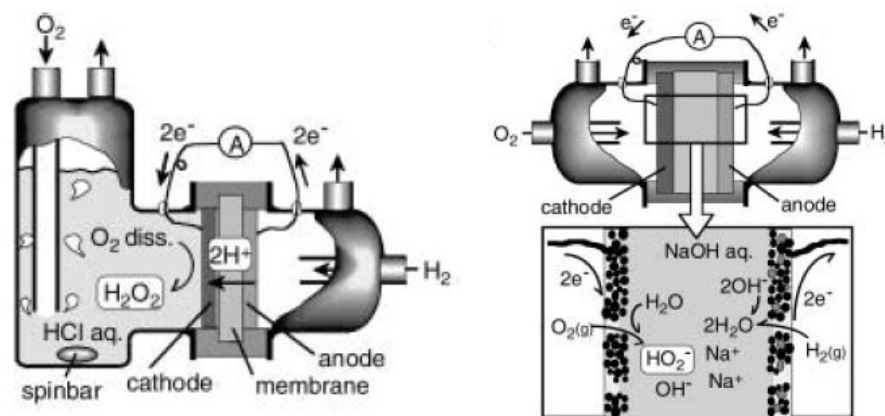
Figure 11   Structure diagram of H_2/O_2 fuel cell for direct synthesis of H_2O_2 used by Yamanaka group. Left (old cell reactor) [165] and Right (new cell reactor) [166] (Copyright © 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

Table 2   Representative experimental results of H_2/O_2 fuel cell method for the direct synthesis of H_2O_2

Cathode	Selectivity of H_2O_2	Concentration of H_2O_2	Electrolyte	Reference
Au-mesh	<50%	0.2%	acidic	[165]
VGCF-XC72-PTFE	94%	7%	alkalic	[166]
Mn-OEP/AC	47%	3.5%	acidic	[167]
Mn-OEP/AC	47%	7.2%	acidic	[168]
CoTPP/VGCF	42%	13.5%	neutral	[169,170]
VGCF-PTFE-AC	40.1%	1.2%	acidic	[171]
CoN$_2$Cx	32%	12%	neutral	[172]
VGCF-XC72	95%	6.9%	alkalic	[173]

Johnson-Matthey studied the synthesis of H_2O_2 by H_2/O_2 fuel cell in acidic condition (perchloric acid electrolyte). One of their patent disclosed some cobalt catalysts supported on active carbon with different loading ($<$ 10 wt%, 2 wt% is preferable) [174]. Using these electrode catalysts and under preferred conditions, 30 wt% H_2O_2 solution could be get, and the cells could be operated in the laboratory for several months without any noticeable loss of performance. In addition, Johnson-Matthey investigated the modification of the cobalt electrode catalysts using amine-complex

[175]. Recently, their another patent disclosed that an activated transition metal-free carbon electrode has been developed and, by using this catalyst, around 11 wt% H_2O_2 solution could be produced continuously. During the investigated 336 h, the reaction results is stable without any loss of performance [176].

In general, under the condition of alkaline electrolyte, high selectivity and high concentration of H_2O_2 solution can be achieved simultaneously. However, in the alkaline H_2/O_2 fuel cell, H_2O_2 product is unstable. That is, H_2O_2 can not be stored in alkaline condition as such the product has to be acidified. Therefore, the reported works in acidic and neutral conditions may be more interesting for application and, they have another big advance of using half-flooded cell for cathodic compartment [165-168, 171]. Another point should be stressed out is that the operating voltage and the current density is relevant and, their arithmetic product is the effective power density. So, under the specific effective power density, the operating voltage and the current density can not be high simultaneously. Indeed, if the current density is too small, the investment needed will be very large thus not acceptable. If the voltage is low (short circuit), little power can be extracted so the fuel cell becomes only a chemical reactor. The effective power density is determined by the catalytic activity of the electrode materials. Therefore, the catalytic performance of the electrode catalytic materials is the key point.

The advantage of H_2/O_2 fuel cell method is that the safety is guaranteed and electricity may be generated when H_2O_2 is produced. Therefore, it is considered to be a green route for direct synthesis of H_2O_2, and it has a good application prospect in the field of environmental protection. But, preparation of high active electrode catalytic materials as well as the synergy of selective electrocatalysis of the cathode and three-phase boundary of O_2 (gas phase), electrocatalyst (solid phase) and electrolyte (liquid phase) should be studied in detail to achieve high current efficiency, high H_2O_2 concentration and more extracted power [177].

2.3 H_2/O_2 plasma method

The H_2/O_2 plasma method for the DSHP usually adopts dielectric barrier discharge (DBD). The DBD reactor is composed of high voltage electrode, dielectric and grounding electrode. The principle of the H_2/O_2 plasma method to synthesize H_2O_2 is: when the intensity of electric field between the electrodes reaches a certain value, gas discharge takes place in the reactor, and the H_2/O_2 gas mixture is transformed into H_2/O_2 plasma. In the plasma, reactant molecules, through inelastic collision with

electrons with high kinetic energy, are activated into active radicals. These radicals, under the condition of ambient temperature and atmospheric pressure, react with each other spontaneously to generate H_2O_2. Structure of the DBD reactor, composition of the gas mixture and discharge parameters are the main factors influencing the result of H_2O_2 synthesis.

2.3.1   Security issue of the H_2/O_2 plasma method for the DSHP

At the beginning of the last century, the former Soviet Union scholar first put forward the H_2/O_2 plasma method for the DSHP; In the 1940s, the German IG Farben company carried out the research of dielectric barrier discharge under atmospheric pressure for the synthesis of H_2O_2, but only 2% H_2O_2 yield were achieved [178]. In the 1960s, Kobozev et al. [179,180] investigated the reaction conditions (temperature, pressure, gas flow rate and power, etc.) of H_2/O_2 DBD for direct synthesis of H_2O_2 and, found that, under the conditions of -35 □~7 □, 0.65 atm, 96.5% hydrogen and 3.5% oxygen, 3.7 to 3.8 L/h (flow velocity) and -73 □ cold trap collector, H_2O_2 solution with the concentration of 80 wt % was achieved. At the same time, Morinaga et al. [181-183] systematically studied the influence of the structure parameters of the wire-cylinder DBD reactor (electrode size and gap), the discharge parameters (discharge voltage, discharge frequency and pulse current) and the filling materials on the synthesis of H_2O_2. The results showed that the gap of electrodes is an important structural parameter, which has significant effects on generation rate and selectivity of H_2O_2. Pulse current is a very important discharge parameter and, H_2O_2 generation rate increases with the increasing of pulse current value. Mg-TiO_2, TiO_2 and $BaTiO_3$ as filling materials will significantly decrease the selectivity of H_2O_2. While B_2O_3 and H_3BO_3 as filling materials have little influence on H_2O_2 selectivity. The above mentioned experimental results indicate that H_2O_2 molecule is stable when it contacts with B_2O_3 and H_3BO_3 (maybe linked to perborrate formation on the surface), which give us some guidance to select materials for design of DBD reactor.

From the early literature reports, the prominent advantage of the H_2/O_2 plasma method is that there is no solvent or catalyst and, H_2O_2 can be synthesized with high selectivity and high concentration under the optimized conditions. In addition, compared with noble metal catalysts, the H_2/O_2 plasma method is featured by its feed composition, that is, hydrogen is excess. However, same as the noble metal catalytic method, H_2/O_2 plasma method also has to consider the safety issue. In the mixture of H_2 and O_2, the explosion limit is very wide (4% ~ 94% H_2 or 6% ~ 96% O_2), thus the early studies usually

adopted H_2/O_2 mixture with oxygen content below 6% as feed gas. However, in industrial applications, H_2 must be recycled. In order to ensure that the O_2 concentration is not higher than 6% during the circulating of H_2, in the 1990s, Mitsubishi company applied for a patent on a device for detection and sensing of gas pressure [184], which was aimed at supplementing and controlling oxygen concentration in the process of hydrogen circulation. However, under the condition of O_2 concentration less than 6%, circulation volume of H_2 is huge and the efficiency of H_2O_2 synthesis is low, which greatly reduce the practicality of the H_2/O_2 plasma method.

In recent years, through design and optimization of plasma reactor, Guo et al. [185-187] have made an important progress in improving security of the H_2/O_2 plasma method for direct synthesis of H_2O_2. The experimental results show that, in a self-cooling double dielectric barrier discharge (SC-DDBD) reactor, H_2/O_2 plasma reaction can safely synthesize H_2O_2 even when O_2 concentration is close to 30 mol % and, the selectivity and yield of H_2O_2 were both greater than 60% [187]. By contrast, in a conventional single dielectric barrier discharge (SDBD) reactor without circulating water cooling, the explosion occurs immediately as long as O_2 concentration in H_2/O_2 mixture is over 6 mol % (as shown in Figure 12), and the selectivity of H_2O_2 is below 1%.
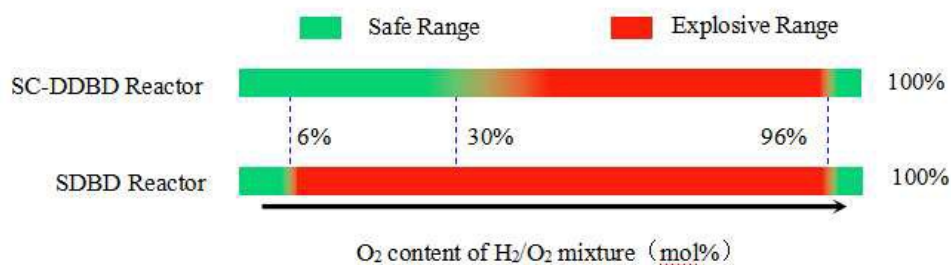

Figure 12   Diagram of reaction safety in the SC-DDBD and SDBD reactor

Recently, Guo et al. [188] developed a multi-tube SC-DDBD reactors (Figure 13), in which the scale-up synthesis of H_2O_2 from H_2 and O_2 can be operated continuously. Using H_2/O_2 mixture with O_2 concentration at 15 mol% as feed gas, reaction process was safe and stable. H_2O_2 solution (65 wt%) can be produced continuously with H_2O_2 selectivity at 67% (as shown in Figure 14). The H_2O_2 solution, analyzed by Inductively Coupled Plasma Emission Spectrum (ICP), was found to be high purity production, in which the content of most impurities meet the SEMI standards (SEMI Grade 2) except B, Ca, Mg, As and Zn, but the five impurities also meet the SEMI Grade 1 standard. At present, under

the optimized conditions, 64 g H_2O_2 solution with the concentration of 10 wt % (diluted by water) can be produced at the energy cost of 1 kW•h. Guo et al. [188] predicted that, the cost of hydrogen (99 %), oxygen (99 %) and electricity for the production of 1 Kg 65 wt% high-purity H_2O_2 is about 85 yuan RMB (9.4% for H_2, 8.2% for O_2, 82.4% for electricity) based on Chinese market prices while the sale price of the similar high-purity H_2O_2 product in Chinese market is about 150 yuan RMB/Kg.

It is estimated that the cost of the DSHP through plasma method is still much higher than that of the traditional AO process. Obviously, the main chance for the plasma method to further decrease the production cost lies in reducing the electricity consumption. In addition, under the etch of H_2/O_2 plasma, how long is the age of the dielectric materials should be studied through long-term experiment, although an invariable experimental results emerged during a 150 h continuous operation. Another point to note is that, as for safety reasons, the electrical power should never be off and on (if the electrical power is only off, the plasma will disappeared and we can shut down the equipment immediately, in this case it is safe; but if the electrical power is off and immediately on, the equipment can not be shut down in time, in this case, the electric field in the plasma reactor will increased sharply in a short period of time, and explosion may happen if the content of O_2 is in the explosive limit), this may cause additional complexity to the power supply and protective equipment.
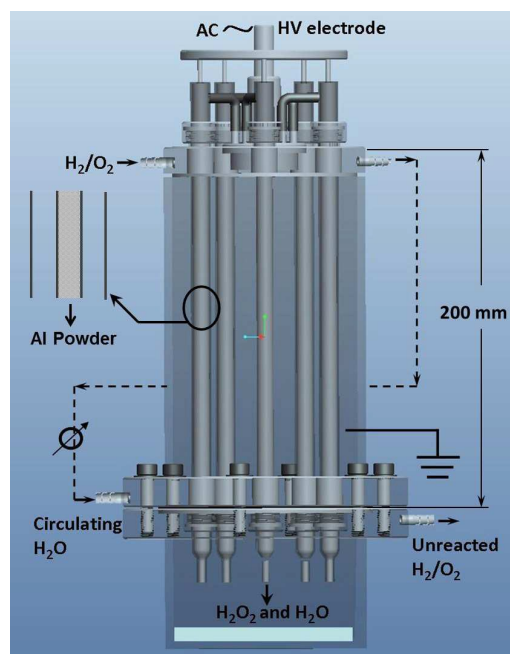

Figure 13   Structure diagram of the multi-tube SC-DDBD reactor (Copyright© 2013 American Institute of
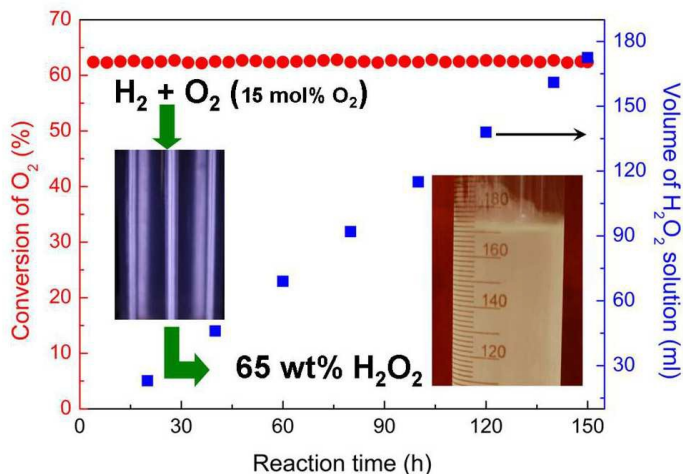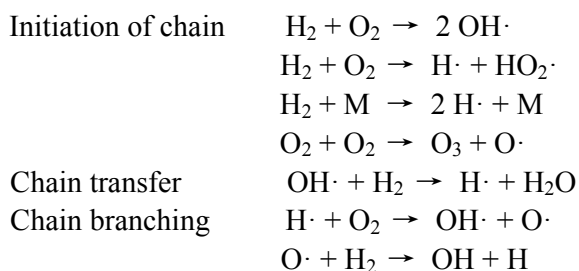
Chemical Engineers) [188]

Figure 14   Reaction results of H_2/O_2 plasma in the multi-tube SC-DDBD reactor (Copyright© 2013 American

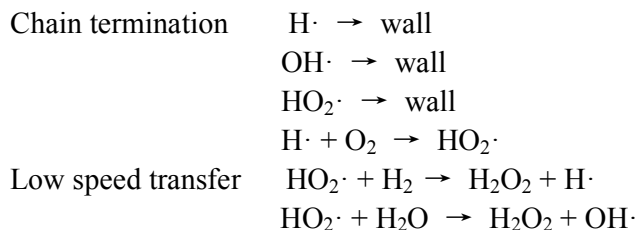Institute of Chemical Engineers) [188]

2.3.2   Reaction mechanism of H_2/O_2 plasma for the DSHP

In order to study the reaction mechanism of H_2/O_2 plasma for the DSHP, the key is to obtain the following information: (1) the formation paths of H_2O_2 and H_2O and the methods to improve the H_2O_2 selectivity; (2) the cause of the explosion in H_2/O_2 plasma and the methods to avoid explosion.

In regard to the formation paths of H_2O_2, the early literature [189] thought that there were two possibilities. One path was recombination of OH free radical (OH· + OH· → H_2O_2), and the other path was the reaction between hydrogen species (H· and H_2) and HOO· or HOOO· species. In addition, Mitsubishi company [184] mentioned that the reaction between hydrogen atom and oxygen molecule could be the main formation path of H_2O_2.

With respect to the cause of the explosion in H_2/O_2 plasma, there has been no literature reports. People's understanding about the explosion mechanism of H_2/O_2 mixture is mainly based on free radical chain reactions at high temperature [190,191]:

Initiation of chain $H_2 + O_2 \rightarrow 2\,OH·$
                           $H_2 + O_2 \rightarrow H· + HO_2·$
                           $H_2 + M \rightarrow 2\,H· + M$
                           $O_2 + O_2 \rightarrow O_3 + O·$
Chain transfer $OH· + H_2 \rightarrow H· + H_2O$
Chain branching $H· + O_2 \rightarrow OH· + O·$
                           $O· + H_2 \rightarrow OH + H$

Chain termination $H\cdot \;\rightarrow\;$ wall

$OH\cdot \;\rightarrow\;$ wall

$HO_2\cdot \;\rightarrow\;$ wall

$H\cdot + O_2 \;\rightarrow\; HO_2\cdot$

Low speed transfer $HO_2\cdot + H_2 \;\rightarrow\; H_2O_2 + H\cdot$

$HO_2\cdot + H_2O \;\rightarrow\; H_2O_2 + OH\cdot$

To sum up, people's understanding about the reaction mechanism of H_2/O_2 plasma, for a long time, is extremely limited. The main reason is that few diagnostic methods can be used for in site study of plasma reaction. In recent years, by using in site Optical Emission Spectrum (OES) diagnostic technique, O^{18} isotopic tracing and Raman Spectrum, we studied the activation process of H_2 and O_2 as well as the plasma reaction mechanism in SC-DDBD and SDBD reactor [187]. Results show that the activation of H_2 in DBD plasma is mainly accomplished by dissociation triggered by cumulative vibrational excitation, and the activation of O_2 is mainly implemented through electronic excitation dissociation. As shown in Figure 15, the formation path of H_2O_2 consists of two steps: the generation of HO_2 intermediate by chain termination reaction from H and O_2 ($H + O_2 \;\rightarrow\; HO_2$) and the generation of H_2O_2 by self-disproportionation of HO_2 intermediate ($HO_2 + HO_2 \;\rightarrow\; H_2O_2 + O_2$); and the formation path of H_2O also includes two steps: the generation of OH active species by chain branching reaction from reactive oxygen species and active hydrogen species ($O + H_2^* \;\rightarrow\; OH + H$ and $H + O_2^* \;\rightarrow\; OH + O$) and the generation of H_2O by chain transfer reaction from OH and H_2 ($OH + H_2 \;\rightarrow\; H + H_2O$). That is to say, activation of O_2 mainly leads to the formation of H_2O, and activation of H_2 mainly leads to the generation of H_2O_2.
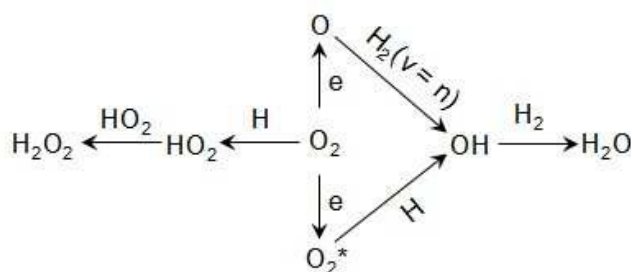

Figure 15   Reaction mechanism sketch of H_2/O_2 plasma for the DSHP (Copyright © 2013 WILEY□VCH Verlag

GmbH & Co. KGaA, Weinheim) [187]

The reaction for generation of OH from reactive oxygen species (O and O_2^*) and active hydrogen

species (H and H_2^*), as well as the reaction for formation of H_2O from OH and H_2 all belong to fast and high exothermic reaction, which is the main cause for explosion of H_2/O_2 plasma. In the SC-DDBD reactor, the H_2/O_2 plasma reaction is highly safe, and the reason is that the SC-DDBD reactor, through uniform and diffuse discharge, can reduce the density of electron, which can further reduce the concentration of reactive oxygen species (O and O_2^*) and active hydrogen species (H and H_2^*). In order to further improve the selectivity of H_2O_2 and the reaction safety, how to avoid the activation of O_2, that is, how to activate H_2 selectively is the research direction in the future.

3 Conclusion and Prospect

In conclusion, based on literature reports, noble metal catalysis, fuel cell and plasma are the three representative approaches for the DSHP from H_2 and O_2. The noble metal catalytic method has the best potential to replace AO process and become a green approach for bulk production of H_2O_2. The future research emphasis is to further develop some more efficient catalysts, select appropriate reaction conditions and solve engineering problems. In regard to the catalysts, Pd is the most efficient active element, which has high activity but low selectivity because of H_2O_2 hydrogenation. In order to improve the selectivity and productivity, Pd should be kept at oxidation state through alloying with some other metals (electron transfer to Au, Pt, Ru, etc), creating some surface oxygen-containing functional groups (on support) as well as strong metal support interaction (capturing electron from Pd); support should have acidity (stabilizing H_2O_2 molecule), low isoelectric points and suitable textural property (high mechanical and chemical stability, also is beneficial to form appropriate Pd crystal plane and particle size). With respect to the reaction conditions, the reaction medium (solvent), side-reaction inhibitor as well as reaction pressure and temperature should be investigated detailed. About the engineering problems, the design of flow reactor is the focus, because it is the key to the safety. In addition, the configuration of the reactor is also important to maximize the yield of H_2O_2, through matching up with the efficient catalysts and appropriate reaction conditions.

The H_2/O_2 fuel cell method is featured by generating electricity during the production of H_2O_2 solution, therefore it has a good application prospect in the field of environmental protection. Its future research will be focused on the preparation of some high-efficiency catalytic electrode materials. The electrode catalysts should not only improve the concentration of H_2O_2 by increasing O_2 pressure on the surface of cathode, improving catalytic activity and reducing the decomposition rate of H_2O_2, but also

be more cheap and easy to make. Therefore, the synergy of selective electrocatalysis of the cathode and three-phase boundary of O_2 (gas phase), electrocatalyst (solid phase) and electrolyte (liquid phase) should be studied in detail to achieve high current efficiency, high H_2O_2 concentration and more extracted power.

The H_2/O_2 plasma method does not use any catalysts or solvents, thus it has a obvious advantage in direct synthesis of high purity and high concentration H_2O_2 (electronic grade H_2O_2 and propellant grade H_2O_2) through a condensation collector. The future research emphasis is, through optimizing the structure of DBD reactor and improving the efficiency of plasma power, to improve energy efficiency and solve some engineering problems in the process of scale-up synthesis. The scale-up synthesis of H_2O_2 by plasma method will be realized by increasing the number of reactor, and the engineering problems include the integration of multi-tube reactor and the matching between the reactor and plasma power. In addition, the current synthesis cost of the plasma method is still much higher than the traditional AO process, thus some more efficient methods to further decrease the electricity consumption should be studied for future application.

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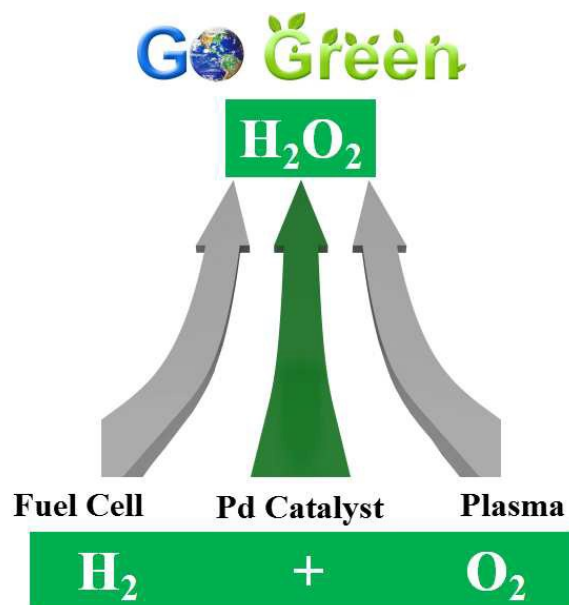
The direct synthesis of H_2O_2 from H_2 and O_2 by Pd catalyst, fuel cell and

plasma have been reviewed systematically.