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To Study of Synthesis of Hydrogen Peroxide using Supported Catalysts

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Abstract: The direct synthesis of hydrogen peroxide (H2O2) from oxygen and hydrogen was investigated in this study using supported catalysts. Compared to the existing industrial production method, the direct path is a more sustainable and environmentally friendly option. To ensure that the direct approach might be economically viable, this research mainly aimed to achieve H2O2 yields and selectivity that met industrial requirements. Meeting this objective necessitated exploring two new approaches to the direct synthesis of H2O2.

Keywords: Catalysts, Synthesis, Hydrogen , Sustainable

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INTRODUCTION

Catalysis is the enhancement of a chemical reaction rate by the addition of a specific material, according to current scientific agreement. An alternate reaction process with a distinct transition state and a lower activation energy (E_a.) is how a catalyst functions. This means that more molecules may reach the transition state, where they can undergo reactions and potentially transform into products, since they have more energy to overcome the energy activation barrier.

Hydrogen peroxide is chemically represented by the symbol H_2O_2. What we have here is a colorless, see-through liquid that mixes well with water. It is possible to distill the water and H_2O_2 to get a 100% pure m/m solution since they do not mix to form azeotropic mixtures while 100% m/m H_2O_2 may be synthesized using fractional distillation, this process is often reserved for research reasons rather than commercial use. In fact, pure H_2O_2 may be necessary for some specialized applications. For instance, NASA is considering using pure H_2O_2 to power rockets as it is safer to handle than liquid oxygen. A variety of reactions as well as the temperatures of synthesis and breakdown of H_2O_2 are possible.

Burning hydrogen peroxide (H_2O_2) produces steam, water, and heat (100.4 KJ mol^{-1}). However, for every 10ºC increase, the rate of H_2O_2 breakdown increases by around 2.3 times, a number of other parameters, such as pH, H_2O_2 concentration, and the presence of stabilizers or contaminants, may also influence this rate. There are a lot of substances that break down H_2O_2, including most transition metals and their compounds and a few organic molecules.

$$\textit{Decomposition of } H_2O_2 \qquad 2H_2O_2 \longrightarrow 2H_2O + O_2$$

Under moderate reaction conditions, a variety of organic and inorganic substrates may be oxidized and reacted with H_2O_2, a very active and adaptable oxidant. With large oxidation potentials, H_2O_2 may react throughout the pH range.

$$\textit{Oxidation by } H_2O_2 \qquad H_2O_2 + M \longrightarrow MO + H_2O$$

Strong oxidizing substances as Ce $(SO_4)_2$, $KMNO_4$, NaClO, and Cl_2 may be reduced by H_2O_2, a powerful reducing agent. Common standards for determining the amount of H_2O_2 are KMNO4 and Ce $(SO_4)_2$.

$$\textit{Reduction by } H_2O_2 \qquad H_2O_2 + R \longrightarrow RH_2 + O_2$$

Additionally, when combined with organic reagents, H_2O_2 may undergo substitution reactions, producing a variety of peroxide compounds. These compounds are widely used in organic material production among other applications.

$$\textit{Substitution reaction by } H_2O_2 \quad H_2O_2 + RX \longrightarrow ROOH + HX$$

Louis-Jacques Thenard, in 1818, made the first discovery of H_2O_2. Since then, its uses have grown significantly, and H_2O_2 is now one of the most significant commodity chemicals used in both the household and the fine chemical industry worldwide. H_2O_2 has several potential applications, including disinfectants, waste water treatment, bleaching, and producing a wide range of beneficial chemicals via green oxidation, its manufacture is essential. Bleaching paper and textiles and making fine chemicals account for around 80% of the one million metric tons of H_2O_2 produced each year.

DIFFERENT METHODS FOR DIRECT H2O2 SYNTHESIS

Many academics have been working to create other ways to produce H_2O_2 because of the issues with the AO process. Although other synthetic methods have been researched, none of them have yet to be used on an industrial basis. Below is a summary of some of the more significant routes.

1. Fuel cells

Fuel cell-based H_2O_2 production is a viable substitute. A number of techniques have been put up for the continuous and direct generation of H_2O_2 in fuel cells. The cathode of this membrane, where O_2 is transformed into hydrogen peroxide, consists of graphite or gold mesh, while the anode is responsible for the oxidation of H_2, is Pt. Fuel cells work by reducing O_2 to H_2O_2 at the three-phase boundary.

Compared to catalytic direct production of H_2O_2, fuel cell devices have two benefits. First, since the electrolyte membrane separates the reagent gases, Direct mixing of oxygen and hydrogen removes the explosive dangers. Secondly, the fuel cell arrangement produces both electric power and H_2O_2 production.

2. The plasma

Preliminary studies indicate that at atmospheric pressure, H_2/O_2 may be transformed into H_2O_2 and H_2O using a subdued electric discharge that generates a non-equilibrium plasma. The plasma technique offers several advantages over conventional methods. The non-explosive regime of H_2O_2 mixtures is attained by the stoichiometry of H2/O2 that maximizes selectivity for H_2O_2, and the plasma method is unique as it occurs in the gas phase and exclusively utilizes the H_2/O_2 feed. Additionally, the plasma approach is a safe, eco-friendly method that efficiently produces an aqueous solution of pure H_2O_2 without the problem of diffusivity constraints.

However, the real H_2O_2 yields recorded with prior plasmas were relatively low (about less than 5%) until very recently. The gas phase reaction of H_2/O_2 non-equilibrium plasma may create H_2O_2 at ambient conditions with a modest yield (32.51%) and strong selectivity (56.25%), as shown further recently by Zhou et al. The usage of a plasma approach has demonstrated significant promise in manufacturing H_2O_2 via the direct synthesis.

3. CO2 that is supercritical

Supercritical CO_2 synthesis of H_2O_2 from H_2 and O_2 has been investigated using homogeneous and heterogeneous Pd-based catalysts, it is preferable to utilize it as the reaction medium rather than other organic solvents. Also, at temperatures over 31 degrees Celsius, CO_2 is miscible with both oxygen and hydrogen, creating a two-phase fluid-solid system. An advantage of this process is that it eradicates or substantially diminishes the mass transfer resistance encountered in the three-phase direct liquid synthesis of H_2O_2 (gas, liquid, and solid). Landon et al. investigated catalysts supported on ZnO for the production of H_2O_2 using supercritical CO_2, which included 5 weight percent Au, Pd, and AuPd. The catalyst that just included Pd was found to be useless in creating H_2O_2 since it only yielded water as a byproduct. However, H_2O_2 generation was seen with the Au/ZnO and Au-Pd/ZnO catalysts, although at moderate rates.

DIRECT H2O2 SYNTHESIS USING PD CATALYSTS

In 1914, The first direct H_2O_2 production patent went to Henkel and Weber. The patent explained how to catalyze the direct production of H_2O_2 from its constituent parts using palladium (Pd) catalysts. The majority of the first research was on directly synthesizing H_2O_2 using Pd catalysts, and it was possible to get high concentrations (> 35 weight percent) by increasing the pressure and mixing H_2 with O in the explosive zone. However, it is quite risky to do such experiments in the explosive zone.

There are two reasons why, after over a century of research, there is currently no economically feasible technique for direct synthesis of H_2O_2. To begin, gas mixtures including hydrogen and oxygen are explosive at concentrations ranging from 5% to 25% v/v. For industrial-scale direct synthesis, the catalyst must have little activity for undesirable side reactions and excellent selectivity for H_2 (> 95%).

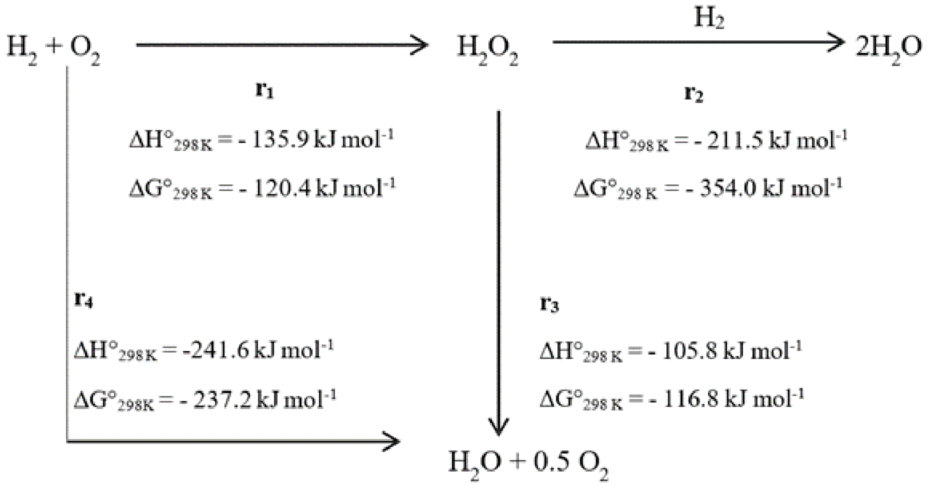

Figure 1. processes by which H_2O_2 is directly produced.

Several patents and papers have shown that acid and halide promoters are superior than Pd-based catalysts for enabling the direct generation of H_2O_2. Pospelova showed in the early 1960s that in order to get a large H_2O_2 production from supported Pd catalysts, acid (HCl, HNO_3) had to be added. There are two possible classifications for acids based on the research: halide acids and oxyacids. Despite the fact that the former group reduced H_2O_2 breakdown activity, the direct synthesis approach produced very little or no H_2O_2. The latter group, on the other hand, significantly improved the selectivity for H_2O_2 production while being powerful suppressive acids.

A substantial body of research underscores the impact of halide incorporation into catalyst structure on H_2O_2 production, with bromide exhibiting the highest activity among halide ions. Lunsford and Choudhary demonstrated that Cl and Br halide ions effectively inhibit the active sites responsible for H_2O_2 breakdown activities. It is thought that these halide ions prevent molecular oxygen from cleaving to produce water.

One active phase for the direct generation of H_2O_2 was shown by Lunsford and Dissanayake to be colloidal palladium. In their experiments, they used Pd/SiO_2 as the catalyst and a highly concentrated HCl solution (1.0 M) as the reaction medium. When HCl was added to $PdCl_2$, Pd_0 was oxidized to generate $PdCl_2$- ions in solution. Adding a lot of acid to the reaction mixture has three drawbacks: (i) it has to be removed later; (ii) it could cause reactor material corrosion, which could compromise operational safety; and (iii) it could dissolve the catalyst's metal active phase into the reaction mixture, making the catalyst and the H_2O_2 it produces unstable. In order to increase the Pd catalysts' efficiency, a new catalytic system must be created.

- **Gold Catalysis**

One of the most important synthetic processes used in the pharmaceutical and fine chemical industries to produce a wide variety of intermediates and products is the selective oxidation of substrates. However, many of these processes are carried out on a commercial scale employing activated forms of O_2 (such

H_2O_2) or stoichiometric oxygen donors (like manganates). Catalytic hydrogenation techniques use molecular hydrogen as a reagent, as opposed to selective oxidation reactions. The selectivity of the reaction may be fine-tuned by avoiding catalyzed hydrogenations in favor of non-catalyzed ones. However, selective oxidation procedures do not work in this way, however, since homogeneous non-catalyzed oxidations may easily compete with the catalyzed process, particularly at high temperatures, because dioxygen is a di-radical in its ground state.

Controlling selectivity is a significant experimental challenge, among the primary causes Using air or dioxygen for small-scale oxidations has not yet done. This highlights how crucial it is to continue developing catalysts for selective oxidation that may be used in conjunction with molecular oxygen.

The subject of gold chemistry has seen significant change during the last several decades. Disproved is the long-held and widely-held notion that gold is a chemically inert metal. In the 1980s, there were two major breakthroughs in the chemical processes that used gold. Even though these results were published in the 1980s, it wasn't until the late 1990s that there was a genuine interest in gold catalysis.

Gold has exceptional activity as a homogeneous or heterogeneous catalyst when it is finely split into nanoparticles composed of just a few hundred atoms. In certain situations, it is even the preferred catalyst, outperforming the catalytic qualities of Group VIII metals. A variety of processes, including selective oxidation reactions including CO oxidation, alcohol oxidation, and direct synthesis for H_2O, are thought to be effectively catalyzed by nanoparticulate gold. Some of the most significant uses for Au nanoparticles that have been effectively implemented are covered in the sections that follow.

- **The Oxidation of Carbon Monoxide**

Controlling CO emissions is crucial since they are a major hazard to the environment and human health in the exhaust gases of automobiles with gasoline or diesel engines as well as industrial operations. Supported Au nanocrystals (less than 5 nm) have been shown by Haruta et al. to oxidize CO at very low temperatures with remarkable efficiency as catalysts. In contrast to catalysts produced using impregnation methods, precipitation-based catalytic materials produced more active catalysts. It was shown that the kind of support and the technique used to prepare the catalyst may significantly impact the catalyst's activity and selectivity, this may cause heterogeneous catalysts' active sites to shift. Active catalysts for CO oxidation are typically small Au crystallites on an oxide substrate, with a diameter of 2-4 nm.

There has been much discussion about the properties of the active sites of these catalysts. As per the theory put forward by Bond and Thomspon, the contact between the oxide and the Au particle contains the active oxidation sites, which are atoms of Au. Although the roles of Au0 and Au3+ have been investigated thoroughly, the exact nature of the catalytic activity of the gold component remains a mystery. The most active size for CO oxidation is tiny Au particles (3-5 nm), and the reaction may be attributed to quantum size effects, according to Goodman et al. The most active and persistent Au particles have a diameter of 1.4 nm and contain five atoms, according to Boyen et al., They also show that Au may serve as the active site for CO oxidation. Furthermore, Norskion demonstrates that the thermodynamically preferred pathway for CO oxidation transpires on 10-atom Au nanoparticles. The function of Au^{3+} has, conversely, been the focus of other research groups. Baker et al. presented a mechanistic theory that supported Bond and

Thomson's assertion that the high catalytic activity is a result of the tiny Au nanoparticles' peripheral effects. Lastly, Hutchings et al. also demonstrated that the key element for CO oxidation in Au/FeO_3 was Au^{3+}.

- **Acetylene hydrochlorination**

The catalyst's active component sublimated, rendering the catalyst inactive, even though it was a major technique for generating vinyl chloride in the early 1980s. Thus, there was a greater need to identify a catalyst for this reaction that was more stable. One of the first investigations to demonstrate that cationic gold may function as an efficient heterogeneous catalyst was the hydrochlorination of acetylene.

This prediction was confirmed by further study by Hutchings, who found that gold was a more stable catalyst than mercuric chloride, however these new catalysts eventually deactivated. Temperature was shown to affect the rate of deactivation, with the lowest deactivation occurring at temperatures of around 100^{o}C. The catalyst was not active enough at this temperature, however, and temperatures of around 180^{o}C are ideal. Deposition of polymeric carbonaceous materials was thought to be responsible for deactivation at temperatures below 100°C, whereas reduction of Au^{3+} to Au0 was thought to be the source of deactivation at higher temperatures. By cofeeding diluted NO in with the reactor fuel, in-situ reactivation prevented the deactivation.

- **Epoxidation of alkenes**

Some of the other products that include PO include solvents, synthetic lubricants, flame retardants, oil drilling chemicals, and textile surfactants. Approximately 3.5 million tons of PO are produced annually worldwide, with a $7 billion annual market. PO is now made commercially utilizing a two-stage chemical reaction using organic peroxides or Cl_2 that produces stoichiometric byproducts.

- **Oxidation of Alcohol**

The capacity to selectively oxidize alcohols is crucial in the fine chemical industry, facilitating the transformation of diverse substrates into ketones and alcohols. Gold nanoparticles may be very efficient in the selective oxidation of alcohols, especially diols such as 1, 2-propanediol, according to pioneering work by Rossi, Prati, and others. Compared to other noble metals, gold catalysts exhibit better activity and selectivity (> 98%).

Direct H_2O_2 synthesis

Basic supports such as MgO and ZnO were found to be unsuitable since they facilitated the unwanted reactions and produced just water, in contrast to the optimal performance of Au/SiO_2.

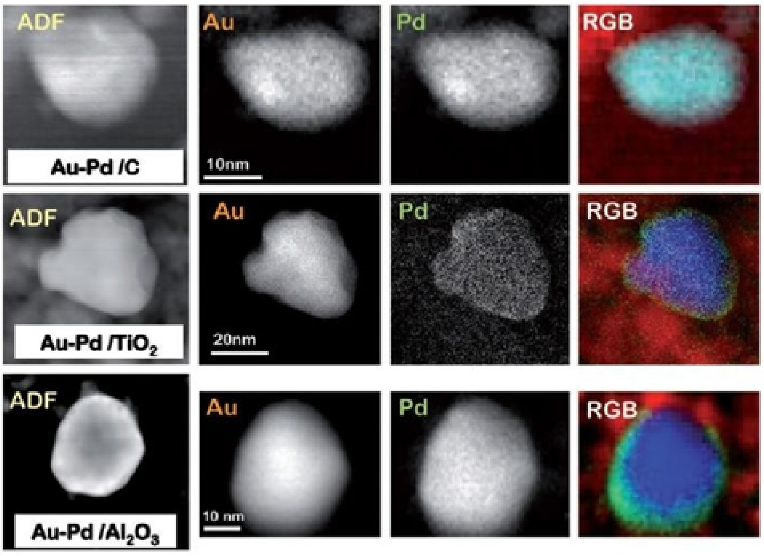

Figure 2. Montage of the HAADF image: calcined catalysts on three supports with Au, Pd, and RGB overlay maps (Au blue, Pd green).

The most frequent competing reactions are known to be the hydrogenation and decomposition processes. We looked into and better understood these conflicting reactions by examining a number of supported monometallic catalysts and bare supports. The Pd supported catalyst showed faster rates of hydrogenation and breakdown than the bare supports. These findings are consistent with earlier research that found Pd-catalyzed H_2O_2 production to be difficult and only successful when accompanied by halide and acid promoters that regulate the conflicting processes.

Hydrogenation and breakdown rates were lower for several Au-supported catalysts compared to their bare supports, indicating that the regions involved in competing processes and direct H_2O_2 production may be separate. These results also showed that gold nanoparticles could be crucial in obstructing the locations of the hydrogenation and competing breakdown processes. The purpose of the gold nanoparticles was to enhance H_2O_2 selectivity by blocking the dissociation sites.

CONCLUSION

The prevailing method for the worldwide production of H_2O_2 is based on the anthraquinone auto-oxidation (AO) process. Over the course of sixty years, this method has been fine-tuned to produce high quantities of H_2O_2 and selectivity for H_2. Nevertheless, the AO method has a number of drawbacks, chief among them being the ongoing need to replenish organic solvents. To do this, H_2O_2 must be produced at a centralized location, supplied in a concentrated state, and then, before to use, diluted with water.

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