*Journal of Advances in Science and Technology*
*Vol. 21, Issue No. 1, March-2024, ISSN 2230-9659*

DOI: https://doi.org/10.29070/2dst7k68

# To Study Metallic Gold Catalyst-Enabled Hydrogen Peroxide Synthesis

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**Abstract:** In this study, we look at the potential for directly monitoring gas-phase H2O2 production in a continuous gas flow reactor. To study how atmospheric and supersonic pressures affect the behavior of gas-phase H2O2 produced directly, we built two lab-scale flow reactors on-site. The results showed that creating H2O2 directly in the gas phase was challenging, and that the stability of the H2O2 was much diminished due to the absence of a solvent. Results show that organic molecules may be gas-phase oxidized using oxygen and gold-palladium nanoparticles; this much is proven. Synthesis rates high enough in the TAP reactor and the fixed bed gas phase reactor allowed for the identification of H2O2 as a product. This finding opens the door to the prospect of directly manufacturing H2O2 via a gas phase approach.

**Keywords:** synthesis, H2O2, Catalysts, temporal analysis, gold-palladium nanoparticles

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## INTRODUCTION

The modern definition of catalysis is the enhancement of a chemical process by use of a catalyst. The activation energy (Ea) of a reaction may be reduced with the help of a catalyst, which essentially creates a new reaction mechanism with a lower Ea. Because of this, there are more molecules with enough energy to undergo reactions and transformations into products because they can reach the transition state and pass the energy activation barrier.

In modern times, catalysis is an essential part of many chemical processes and plays a significant role in both daily life and the economy. Using a catalyst is essential at least once in the manufacture of 90% of all compounds. Catalysts are used by the fuel industry to transform oil into diesel and petrol by "cracking" and "reforming" the oil. Hydrogenation of unsaturated oils and polymerization of liquids into polymers are two of the many processes that rely on catalysts in the food industry. With each passing year, catalytic processes continue to produce goods worth about $900 billion throughout the globe. Many processes may be improved in terms of speed, cleanliness, and sustainability by a knowledge of and careful use of catalysis.

Catalysis may be broadly classified into three types: biological, homogeneous, and heterogeneous. Enzymes are a kind of biological catalyst that occurs spontaneously in all living things. In an enzyme-catalyzed reaction, the substrate is the reactant that first undergoes chemical transformation to produce the end product. Enzymes, the most majority of which are proteins, catalyze over five thousand different kinds of biological reactions.

There are a variety of established principles that may guide the planning, creation, and execution of chemical goods and procedures. Engineers and scientists may safeguard and improve the economy by adhering to these principles, people and the earth via the development of novel approaches to waste reduction, energy conservation, and the identification of safer alternatives to harmful chemicals.

The selective oxidation of substrates is an essential synthetic technique used in the pharmaceutical and fine chemical industries to produce various intermediates and final products. However, many of these reactions are carried out on a commercial scale utilizing oxygen donors that are stoichiometric, such as manganates, or activated forms of oxygen, such as $H_2O_2$. Catalytic hydrogenation uses molecular hydrogen as a reagent, which is different from selective oxidation reactions. When comparing hydrogen and dioxygen as reagents, their activities are the most important consideration. Hydrogen activation on a heterogeneous catalyst surface is an essential initial step in the hydrogenation process. Reaction selectivity can be fine-tuned since uncatalyzed hydrogenations don't exist to compete. Because dioxygen in its ground state is a di-radical, homogeneous non-catalyzed oxidations have the potential to overwhelm the catalyzed process, particularly at high temperatures. But selective oxidation procedures are an exception to this rule.

Because of the difficulty in controlling the reaction's selectivity, oxidations in dioxygen or air on a small scale have not been used. Because of this, research into the creation of selective oxidation catalysts for usage in conjunction with molecular oxygen is crucial. Actually, gold catalysts on supports are powerful oxidation reaction catalysts, and gold nanoparticles are effective at selectively oxidizing carbon monoxide, epoxidizing alkenes, and oxidizing alcohols.

For a long time, gold was thought to as a harmless metal, appreciated primarily for its aesthetic value and its use in jewelry. Consequently, catalysis and chemical processes never made use of gold. Despite Bond et al.'s claim that gold nanoparticles may facilitate dienes' hydrogenation, further research indicated that palladium and platinum catalysts were more effective, making gold an unattractive substitute.

The study of gold chemistry has seen tremendous change within the last few decades. We can now say that the long-held and widely-accepted belief that gold is a chemically inert metal has been proven wrong. When it came to using gold in chemical processes, two major breakthroughs occurred in the 1980s. Nanoparticle gold was described as a heterogeneous catalyst by Haruta and Hutchings. Hutchings foretold and subsequently confirmed that gold was the optimal catalyst for acetylene hydrochlorination, and Haruta documented its use in low-temperature CO oxidation. While these results were published in the 1980s, it wasn't until the late 1990s when gold catalysis really started to get attention. Figure 1 shows the exponential growth in the number of publications and patents pertaining to gold catalysis since then.

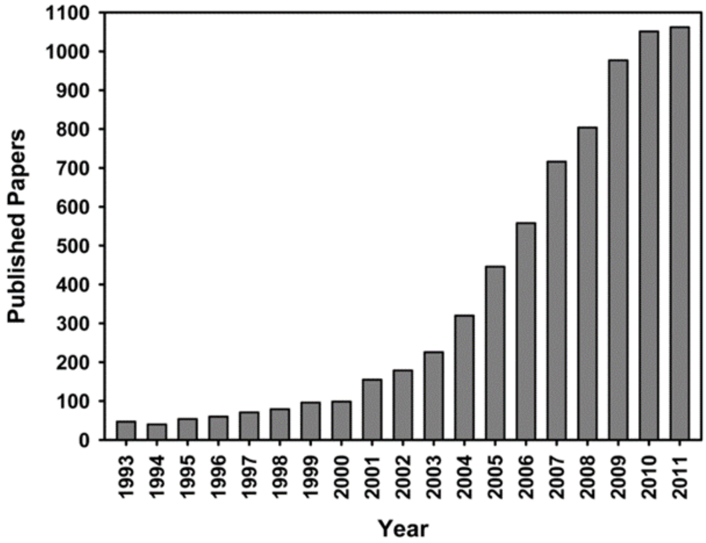


**Figure 1 Research articles published on the subject of "Gold catalysis" (retrieved from Scifinder)**

For both homogeneous and heterogeneous catalyst applications, gold exhibits exceptional activity when reduced to nanoparticles composed of hundreds of atoms or less. In certain instances, this makes it the preferred catalyst, even outperforming Group VIII metals in terms of catalytic characteristics. Many different processes may be catalyzed by nanoparticulate gold, including selective oxidation reactions including CO oxidation, alcohol oxidation, and direct production of $H_2O$. The following sections provide a brief overview of a few of the most significant uses of Au nanoparticles.

## EXPERIMENTAL

### Materials

### Chemical building blocks for catalysts (provided by Johnson Matthey)

The product is a combination of palladium chloride ($PdCl_2$) and hydrogen trichloroauric acid ($HAuCl_4.3H_2O$), with an assay of 41.21% gold.

### Samples of chemicals

Stabilized 50% $H_2O_2$ in water (Aldrich), Decan-1-ol (Aldrich), HPLC Chromasolve (Aldrich) water, methanol (HPLC, Aldrich). Solvesso, Sextate, and Diisobutyl Carbinol are all manufactured by Solvay.

### Catalyst Preparation

### Creating catalysts supported by AuPd by wet impregnation

By wet impregnating different supports, AuPd bimetallic catalysts were created. A typical mixture of 2.5 weight percent gold and 2.5 weight percent Here is the description of the Pd assisted catalyst. 0.0417 g of $PdCl_2$ and $HAuCl_4.3H_2O$ were mixed together. Stirring the mixture and heating it to 80 °C dissolved the $PdCl_2$ to create a uniform solution. After adding the correct support (0.95 g), the mixture was stirred to form a paste. Following a calcination period of three hours at 400 °C (20 ºC min-1), The material was heated to 110 °C and left in an oven for 16 hours to dry.

### Catalyst evaluation

A 100-cc nominal volume, 14 MPa maximum working pressure, stainless steel autoclave from Parr Instruments was used for catalyst testing. An overhead stirrer with a speed range of 0-2000 rpm and a way to detect pressure and temperature were also included in the autoclave. A cooling jacket was used to keep the reaction temperature constant. The autoclaves were linked to cylinders of pre-mixed gas.

### Hydrogenation and breakdown of standard $H_2O_2$ under standard circumstances

The hydrogenation of H2O2 was assessed by loading the autoclave with a catalyst (0.01 g) and a solution of organic solvent and water that contained 4 weight percent H2O2 (0.33 g of 4 weight percent H2O2, 8.17 g of organic solvent). Following three purges at 100 psi, the autoclave was subsequently pressurized to 420 psi with a mixture of 5% H2/CO2. Following the decrease in temperature to 25 °C or 10 °C, the reaction mixture was maintained under stirring at 1200 rpm for a duration of thirty minutes. To quantify the concentration of hydrogenated H2O2, aliquots were titrated using acidified Ce (SO4)2 (1.18 x 10-2 mol L-1) at both the initial and final stages. Solutions of cerium sulfate were compared to a solution of ferroin in a $(NH_4)2Fe\ (SO_4)26H_2O$ standard.

## RESULT

### Analytical techniques

After doing the $H_2O_2$ vaporization and blank tests, the next step was to try to create gaseous $H_2O_2$. Prior to this, a number of catalysts were produced via sol immobilization and assessed for their efficacy in the autoclave system for direct production of $H_2O_2$by Pritchard et al. The sol immobilization catalysts were 50% more active than the impregnation catalysts, and they were quite active overall. In addition, the hydrogenation/decomposition rate of $H_2O_2$was about three times faster than the synthesis process. In fact, as compared to impregnated catalysts, sol immobilization catalysts show far higher hydrogenation activity in the liquid state. But these catalysts are good candidates to investigate in a CGF because of their high $H_2O_2$ productivities. Because, as mentioned in the introduction, the flow reactor's short residence durations should reduce the impact of later events involving hydrogenation and breakdown.

**Table 1 0.5 wt. % catalytic results 0.5 wt.% Au/Pd/Carbon sol-immobilized in H2O2-water trap.**

| Reaction time (h) | $H_2O_2$ observed (g) |
|---|---|
| 0.5, 1, 2, 4, 6, 8, 12, 24, 48, 7 | 0 |

Conditions for a reaction with 50 ml min-1 of H2/air and atmospheric pressure, catalyst weighing fifty milligrams Duration of residence: 1.98 seconds, reaction time: X hours.

Completed solution titrated with acidified Ce (SO4)2 determined H2O2.

Direct $H_2O_2$ generation was examined throughout a temporal range of processes. But zero $H_2O_2$ was still detected after seventy-six hours. For low quantities of $H_2O_2$, the existing water trap was believed to be insufficient. Low amounts of $H_2O_2$ are likely to result from direct synthesis. Water trap efficiency may be compromised or the $H_2O_2$ may be escaping into the vent line, making it impossible to capture effectively. H2O2 is effectively trapped by replacing the water trap with an acidic solution containing potassium titanium oxalate. Solvay® chemically captures hydrogen peroxide with this solution. A [Ti- $H_2O_2$] complex forms instantly when Ti (IV) ions interact with $H_2O_2$; this complex has a yellowish-orange hue and can be measured at 410 nm using a UV-Vis spectrophotometer.

Direct synthesis tests were performed employing the sol immobilized catalyst with $Ti^{4+}$ solution instead of $H_2O_2$ water trap. Table 1 displays the outcomes 2.

**Table 2 Catalytic findings for a solution of 0.5 weight percent gold and half weight percent palladium in carbon - immobilization technique and the $Ti^{4+}$ trap.**

| Reaction Time (h) | $H_2O_2$ observed (g) |
|---|---|
| 0.5, 1, 2, 4, 6, 12 ,24, 48, 76 | 0 |

Conditions for a reaction Under atmospheric pressure, with an H2/air ratio of 2% (50 ml min-1), a catalyst equivalent to 50 milligrams Reaction time: X hours, residual: 1.98 seconds. Spectroscopic $H_2O_2$ determination.

$H_2O_2$ generation was not seen during many direct synthesis procedures using the sol immobilized 0.5 wt. % Au - 0.5 wt. % Pd / Carbon. observed (table 2). The catalysts tested may have struggled at these reaction conditions. Further study examined the influence of flow rate on $H_2O_2$ generation.

## The effect of flow rate

By varying the carrier gas flow rate, we were able to examine the impact of flow rate on product yield, and by extension, the impact of residence time. Experimental conditions included a sol immobilized catalyst with 0.5 weight percent gold and half weight silver/chromium, and the temperature was kept at room temperature. Between twenty-five and one hundred milliliters per minute (ml/min) of carrier gas was used. Table shows the relationship between product yield and carrier gas flow rate 3.

**Table 3 Results obtained from the $Ti^{4+}$- $H_2O_2$-trap**

| Entry | Flow rate (ml $min^{-1}$) | Residence time (s) | H2O2 produced (g) |
|---|---|---|---|
| 1 | 25 | 3.94 | 0 |
| 2 | 50 | 1.97 | 0 |
| 3 | 75 | 1.31 | 0 |
| 4 | 100 | 0.98 | 0 |

Conditions for a reaction Under atmospheric pressure, with an H2/air ratio of 2% (X ml min-1), a catalyst dosed at 50 mg X seconds for residence duration and 80 hours for reaction time. H2O2 content was determined via spectroscopy.

Using sol immobilized catalysts to investigate direct $H_2O_2$ synthesis at varying gas flow rates did not provide any evidence of gas phase production of $H_2O_2$. This disproved the idea that these materials would work well in a continuous gas flow reactor to create H2O2 directly. The catalysts' synthesis may explain their ineffectiveness. Sol immobilization begins with HAuCl4 and PdCl2 dissolved in a mild solution with a stabilizing ligand like polyvinyl alcohol using PVA as a coating prevents the nanoparticles from sintering during the subsequent steps of manufacturing. The next step is to blend homogenous AuPd nanoparticles into a colloidal solution by using a reducing agent. This solution may subsequently be easily applied onto the supports.

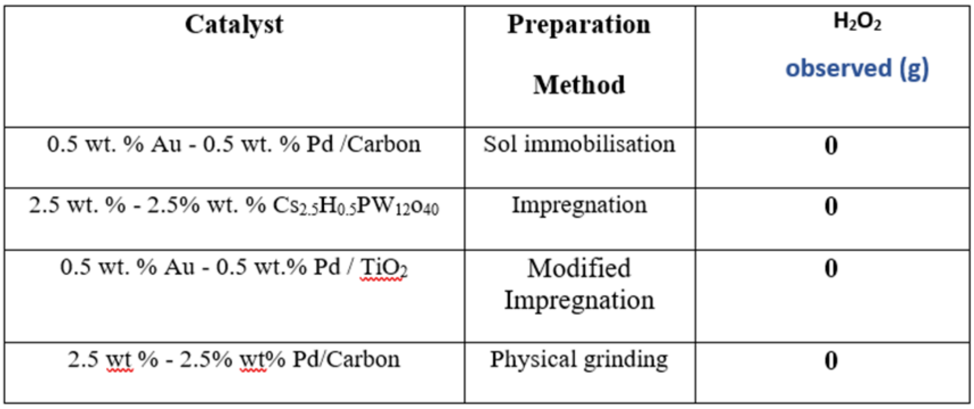
During the preparation process, the stabilizing ligand is left on top of the immobilized nanoparticles. Once metal nanoparticles are bound to a solid support, the stabilizing ligand is usually superfluous. A recent paper highlighted the stabilizing molecule's potential to disrupt gas phase processes by interfering with catalysis. This explains why the sol immobilization catalyst has not been employed to directly produce H2O2 in gas phase. PVA blocks access to the supported nanoparticles' active metal sites, inhibiting the catalyst's activity in direct gas phase H2O2 generation.

## The effect of catalyst

Factors that greatly influence catalysts supported by Au-Pd include their structure, activity, dispersion, particle size distribution, and the technique of production. Much research in recent years has focused on the implications of different preparation techniques on direct synthesis of H2O2. The activity of catalysts created via sol immobilization is greater than that of catalysts manufactured by conventional impregnation techniques, as shown by Pritchard et al. A study conducted by Sankar et al. shown that a little adjustment to the traditional impregnation procedure may enhance the gold's dispersion, leading to a boost in $H_2O_2$ production. The $HAuCl_4$ and $PdCl_2$ are dissolved in water using this modified impregnation process, which also involves the addition of aqueous HCl. Once the support has dried, it is impregnated with this solution. An $H_2$ reduction method is used to extract the halide from the substance. The metal acetate salts were physically mixed to form supported AuPd bimetallic catalysts, which were then heated under He, as described by Kondrat et al. Particular redox reactions, such benzyl alcohol oxidation, benefit more from these chloride-free catalysts than from their impregnated counterparts.

The direct liquid-phase creation of H2O2 using AuPd catalysts based on heteropolyacids has proven very successful, as stated in the previous chapter. Results of direct gas phase production of H2O2 utilizing different AuPd aided catalysts are shown in Table 4, generated using the synthesis methodologies mentioned earlier.

**Table 4 Catalytic activity in a gas flow reactor that continuously produces hydrogen peroxide in the gas phase.**



| Catalyst | Preparation Method | $H_2O_2$ observed (g) |
|---|---|---|
| 0.5 wt. % Au - 0.5 wt. % Pd /Carbon | Sol immobilisation | **0** |
| 2.5 wt. % - 2.5% wt. % $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ | Impregnation | **0** |
| 0.5 wt. % Au - 0.5 wt.% Pd / $TiO_2$ | Modified Impregnation | **0** |
| 2.5 wt % - 2.5% wt% Pd/Carbon | Physical grinding | **0** |

Conditions for a reaction: Here are the necessary conditions: 50 milliliters per minute, 50 milligrams of catalyst, atmospheric pressure, and 2% H2/air. The residence time is 1.98 seconds, while the reaction time is 80 hours. $H_2O_2$ measurement using spectroscopy.

According to Table 4, There was no effect of the catalyst preparation method. on the gas phase's rate of $H_2O_2$ production. Despite testing catalysts that are known to be very active in the liquid phase of H2O2 direct synthesis, no H2O2 generation was discovered in the gas phase. Before H2O2 reaches the H2O2-trap, it may be destroyed by the catalyst, which would explain the lack of production.

### Assessing H2O2 degradation catalyst and support activities

Figure 3 illustrates the steps of testing the catalyst's catalytic activity towards H2O2 breakdown by introducing it into the reactor and screening it for H2O2 degradation.

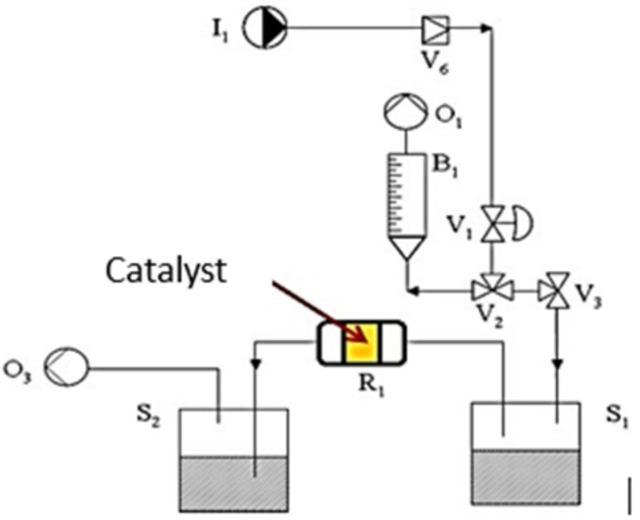


**Figure 3 Catalyst activity evaluation schematic for H2O2 degradation.**

As part of the breakdown experiments, the reactor received a 0.01 g catalyst bed supported by quartz wool. We compared the findings of the catalysts' $H_2O_2$ decomposition reactions to the calibration curve we got from our vaporization tests to see how well they worked. Table 1 displays the outcomes of various decomposition tests 5.

**Table 5 Disintegration of hydrogen peroxide gas over different substrates.**

| Entry | Material | $H_2O_2$ Decomposition (%) |
|---|---|---|
| **1** | .5 wt. % Au – 0.5 wt.% Pd/Carbon[a] | **75** |
| **2** | 2.5 wt. % Au - 2.5% wt. % Pd/ $Cs_{2.5}H_{0.5}PW$ o [b] | **89** |
| **3** | 2.5 wt % - 2.5% wt% Pd/TiO [c] | **89** |
| **4** | 2.5 wt % - 2.5% wt% Pd/Carbon[d] | **73** |
| **5** | Quartz Wool | **0** |

Conditions of reaction Industrial air gas. 0.01g catalyst, 25ºC. Titrating H2O2-water solution with acidified Ce $(SO_4)_2$ determines $H_2O_2$.

a) Catalyst prepared using sol immobilization technique

b) A catalyst that has been created by means of moisture Embryo transfer.

c) Made using a modified impregnation method, the catalyst

d) Physically ground catalyst

All catalysts showed a decrease of around 75% to 90% in $H_2O_2$. Additionally, the evaluation for H2O2 decomposition was conducted on quartz wool, and no $H_2O_2$ loss was observed. Since the reactor and quartz wool are impervious to $H_2O_2$ degradation, catalysts are the only viable option for this process.

Since the catalysts supported by AuPd were able to decompose around 75% to 90% $H_2O_2$, the capacity of various supports to degrade $H_2O_2$ was evaluated. The support was inserted into the reactor and screened for $H_2O_2$ degradation between the water trap (S2) and $H_2O_2$ saturators (S1) to achieve this. The research set out to identify a support that would not breakdown $H_2O_2$ to a significant degree. A catalyst supported by AuPd may be manufactured using this support, and Possibilities for direct gas phase production of H2O2 were then considered. The results of the evaluation of several supports are shown in Figure 4.

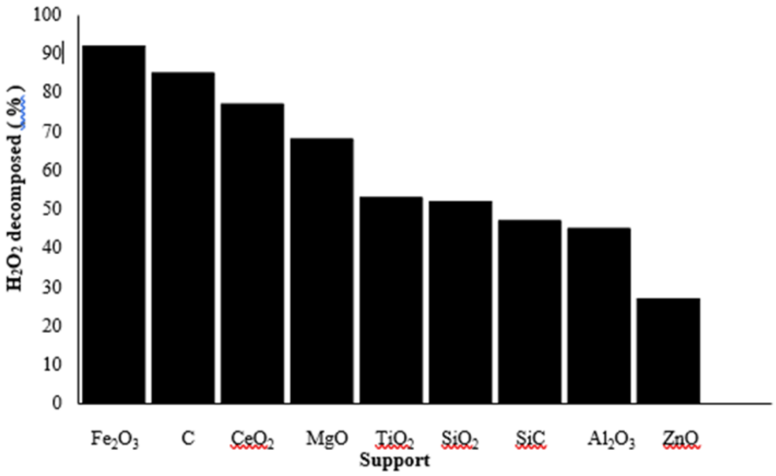


**Figure 4 The gas phase breakdown of hydrogen peroxide over different catalyst support materials.**

Reaction requirements Experimental parameters: temperature (25 °C), flow rate (145 ml min-1), reaction duration (30 min), and support (0.01g). One way to determine the concentration of H2O2 in a solution is to trihydrate it with acidified Ce (SO4)2.

In the gas phase reactor, we tested a number of different support materials for H2O2 breakdown activity. These materials have a history of being used as heterogeneous catalysts for holding nanoparticles of gold, palladium, and autoxide. Figure 4 demonstrates that a considerable amount of H2O2 breakdown was seen in almost all of the tested supports. These findings ran counter to what was seen during the liquid phase of breakdown. This occurs because, unlike in the liquid phase, As the catalyst moves across it, it comes into contact with very concentrated levels of H2O2.

## CONCLUSIONS

The primary objective of this study was to demonstrate that a continuous gas flow reactor can directly generate gaseous H2O2 from hydrogen and oxygen at ambient pressure. Epoxidation of propene in the gas phase utilizing Au/TS1 catalysts reportedly requires the generation of H2O2 from H2 and O2 in the gas phase. Although H2O2 is not commonly regarded as a waste product, it is essential in the oxidation of propene-to-propene oxide. This significant commodity chemical is utilized in the synthesis of polyols and polyurethane.

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