
Synergistic Catalysis: Investigating H₂O₂ Production over Mesoporous Carbons Supported Bimetallic Au-Pd Nanoparticles

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Abstract: Developing catalytic processes to directly produce hydrogen peroxide from molecular oxygen and hydrogen is necessary for the commercialization of hydrogen peroxide as a green oxidant. Bimetallic Au-Pd nanoparticles supported on sequential CMK-3 carbon catalyst that had been acid-pre-treated showed high H₂O₂ production and high H₂ selectivity (>99%). Stable particles with a size of about 2 nm are produced when nanoparticles are encapsulated in the pore network. The introduction of gold is facilitated by metal to metal dispersion, but more significantly, it lowers the H₂O₂ dissociation balance, which is critical for process economy. Hydrogen Peroxide Synthesis and Catalyst Design. Hydrogen peroxide (H₂O₂) is a green oxidant with high atomic economy and environmental benefits. Balancing selectivity and activity for DSHP is challenging due to side reactions and mass transfer limitations. Combining theoretical understanding with controllable nanocatalyst synthesis can facilitate the design of "dream catalysts." Factors affecting catalyst performance include catalyst support, active component, and atomic impurity. The coupling of DSHP and other oxidation reactions is crucial for one-pot in situ oxidation reactions.

Keywords: Hydrogen Peroxide; Direct Synthesis; Aupd Alloys; Nanoparticles; Acid Treatment.

1. Introduction

The pursuit of efficient and selective processes for the production of hydrogen peroxide (H₂O₂) continues to be a focal point in the field of catalysis. This is due to the fact that the compound has a wide range of applications across a variety of industries. Hydrogen peroxide is an essential reagent that is utilized in a wide variety of settings, including environmental remediation and the pharmaceutical industry. Within the realm of synergistic catalysis, this study investigates the catalytic capabilities of mesoporous carbons supported bimetallic Au-Pd nanoparticles for the production of hydrogen peroxide. This is done in order to address the challenges that are associated with traditional synthesis methods.

The passage provides an overview of the challenges and advancements in the direct synthesis of hydrogen peroxide (DSHP) using nanocatalysts, emphasizing the importance of combining theoretical understanding with controllable catalyst synthesis for designing efficient catalysts. Here's a breakdown and summary of the key points:

Hydrogen peroxide (H₂O₂) is recognized as a green oxidant with wide applications. DSHP offers advantages in terms of high atomic economy and environmental friendliness but faces challenges due to side reactions and mass transfer limitations.

Nanocatalysts offer promise for improving DSHP by enabling precise control over catalyst properties. Theoretical insights combined with experimental synthesis techniques can aid in designing optimal catalysts.

The study reviews and discusses various factors influencing catalyst performance, including catalyst support, active components, and atomic impurities. Understanding these factors is crucial for designing effective catalysts.

Catalyst Design Strategies:

Catalyst Support: Optimizing the support material is essential for enhancing catalytic activity and selectivity.

Active Component: Designing the active component of the catalyst is crucial for achieving high efficiency in DSHP.

Atomic Impurities: Controlling atomic impurities can impact catalyst performance and selectivity.

Coupling DSHP with Other Reactions: The study highlights the significance of coupling DSHP with other oxidation reactions to enable one-pot in situ oxidation reactions. This approach can streamline processes and enhance efficiency in hydrogen peroxide production.

Overall, the review emphasizes the importance of understanding catalyst behavior at the atomic level and leveraging nanotechnology to design efficient catalysts for DSHP. Additionally, the coupling of DSHP with other reactions presents opportunities for further advancements in hydrogen peroxide synthesis.

Bimetallic catalysts have emerged as promising candidates for catalytic applications. These catalysts take advantage of the unique characteristics of individual metals to generate synergistic effects that improve the overall performance of the catalytic process. In this particular setting, the combination of palladium (Pd) and gold (Au) nanoparticles supported on mesoporous carbons presents an intriguing avenue for research to investigate. Not only does the mesoporous carbon matrix offer a sturdy support structure, but it also makes it easier for reactants to be transported to the catalytic sites and facilitates increased mass transfer.

It is necessary to have a comprehensive understanding of the structural, morphological, and compositional characteristics of bimetallic catalysts in order to design and synthesize them in a rational manner. The purpose of this study is to investigate the complex interaction that occurs between the bimetallic Au-Pd nanoparticles and the mesoporous carbon support during the process of H₂O₂ synthesis. This will be accomplished by conducting a thorough investigation of these aspects. By shedding light on the mechanisms of catalysis and enhancing the conditions under which reactions take place, our goal is to make a significant contribution to the larger community of catalysis researchers.

In addition, the investigation includes a comparative analysis, which compares the performance of the newly developed catalyst to that of existing alternatives that have been reported in the literature. These comparisons will shed light on the unique advantages and challenges posed by the mesoporous carbon-supported bimetallic Au-Pd system, thereby paving the way for decisions that are informed regarding the potential applications of this system.

The outcomes of this study hold promise not only for advancing the fundamental understanding of bimetallic catalysts but also for addressing the growing demand for sustainable and efficient catalytic processes in contemporary industrial contexts. As we embark on this exploration of synergistic catalysis for the production of hydrogen peroxide, the outcomes of this study hold promise.

2. Methodology

Palladium-based catalysts are currently the most effective for direct synthesis. To maximize reaction efficiency and hydrogen utilization, various preparation techniques, additives, carriers, and reactions have been studied. It is possible to increase the catalytic activity of palladium-based catalysts by alloying palladium with two other metals, particularly gold.[1] Though in practice it is difficult for pure gold catalysts to produce hydrogen peroxide, calculations show that gold catalysts can produce more hydrogen peroxide than palladium-based catalysts. Consequently, even though the exact function of gold is unknown, it plays a significant and frequently linked role in enhancing the bimetallic AuPd catalyst's performance.[2] Palladium is better distributed when gold is present. Additionally, heat changes the electrical properties of the palladium surface. ii. Highly explosive bimetallic AuPd particles form, which appears to decrease the dissociation of hydrogen peroxide formation. iii. Au's capacity to produce hydroperoxides, or precursors of hydrogen peroxide. iv.[3]

Catalysts were created experimentally using SBA-15 mesoporous silica and furfuryl alcohol containing oxalic acid at 30°C. The catalysts were then cured in helium at 300°C for an hour and 850°C for four hours. Place a carbon order. After the silica template was removed from the powder by filtering it with concentrated sodium hydroxide, it was thoroughly cleaned three times using acetone and a large amount of deionized water.[4] At 90 °C, the resultant CMK-3 carbon was air dried. For comparison, NORIT's disordered mesoporous activated carbon was also utilized. As previously mentioned, both positive and negative carbon monoxide were employed as supports, either raw or first treated with nitric acid. Ordered/treated, ordered/untreated, unordered/treated, and unordered/untreated carbon supports were the four types that were typically used.[5] The first step in creating gold, palladium, and gold/palladium catalysts is to wet impregnate the four catalysts with various carbon supports

and metal aqueous solutions. After stirring, the slurry evaporated at 80 °C. Without first filtering, palladium chloride (PdCl₂) and gold chloride (HAuCl₄.3H₂O) from Sigma Aldrich were utilized as metal precursors.[6]

Techniques for characterization

A Micromeritics ASAP 2020 unit was used to analyze the N₂ adsorption properties at 196 °C following the degassing of the activated carbon support and catalyst at 150 °C. To estimate surface area (SBET), the Brunauer-Emmet-Teller (BET) method was employed.[7] At a comparatively high level of 0.05-0.25, there is a lot of data. The Barrett-Joyner-Halenda (BJH) method was used to calculate the mesopore volume and pore size distribution, which were then applied to the desorption branch of the N₂ adsorption isotherm. To characterize the surface chemistry of all catalysts, calcination experiments were conducted in a fixed-bed reactor connected to a mass spectrometer (Thermostar, Balzers). In these experiments, a 50 ml/min argon flow rate was used to heat 100 mg of sample to 950°C.

Analytical examinations

A 250 mL stainless steel autoclave reactor loaded with catalyst (75 mg) and solvent (75 ml of methanol, 0.04M HCl) was used to synthesize the hydrogen peroxide reactions. After that, hydrogen was pumped out of the reactor three times. The autoclave was filled with a mixture of H₂/O₂/Ar (5/10/85%) at 20 bars of pressure once the temperature (5°C) was stable.[8] At 1000 rpm, a four-propeller stirrer was employed to guarantee the right mixture. Cerium sulphate titration was used to measure the concentration of hydrogen peroxide. To ascertain hydrogen selectivity following reactions, gas chromatography was used to analyze the gas phase. Without the catalyst, there was no conversion.[9]

3. Result and Discussion

Table-1: Physical and catalytic properties of the carbon supports.

Carbon support	Pre-treatment	Catalytic Performance		S _{BET}	V _{Mesopore}	d _{pore}
		H ₂ O ₂ Synthesis	H ₂ O ₂ Decomposition	M ² g ⁻¹ ^e	[Cm ³ g ⁻¹] ^d	[nm] ^d
NORIT	HNO ₃ Treated	<0.1	0	1300	0.44	4.6
NORIT	Untreated	<0.1	0	1211	0.46	4.6
CMK-3	Untreated	<0.1	0	1163	0.80	3.3
CMK-3	HNO ₃ Treated	<0.1	0	975	0.70	3.4

- Productivity to H₂O₂ after 60 min, Reaction conditions in text;
- Decomposition of H₂O₂ after 60 min, reaction conditions in text;
- BET surface area from the N₂ adsorption isotherm;
- Calculated using the BJH method to the desorption branch of the N₂ adsorption isotherm

Table-2: Textural properties obtained from N₂ adsorption isotherm data for Au, Pd and Au-Pd catalysts.

Catalyst	Metal Loading, Wt%		Carbon Treatment	Order	S _{BET}	V _{Mesopore}	d _{pore}
	Au	Pd			M ² g ⁻¹ ^e	[Cm ³ g ⁻¹] ^d	[nm] ^d
AO20	5.0	0	2 wt % HNO ₃	Yes CMK-3	815	0.54	3.5
AP	2.5	2.5	Not Treated	No	980	0.53	4.5
AP20	2.5	2.5	2 wt % HNO ₃	No	897	0.49	4.6
APO	2.5	2.5	Not Treated	Yes CMK-3	822	0.54	3.4
APO20	2.5	2.5	2 wt % HNO ₃	Yes CMK-3	860	0.54	3.4
APO20-B	4.0	1.0	2 wt % HNO ₃	Yes CMK-3	847	0.54	3.5
APO20-C	1.0	4.0	2 wt % HNO ₃	Yes CMK-3	862	0.54	3.4
PO20	0	5.0	2 wt % HNO ₃	Yes CMK-3	854	0.54	3.4

- a. Nomenclature of the catalysts.
- b. Surface area from the N₂ adsorption isotherm using BET method
- c. Calculated using the BJH method to the desorption branch of the N₂ adsorption isotherm

The four carbon supports used in this study are summarized in Table 1. Regardless of whether they are ordered or non-ordered, untreated or acid-treated, all supports exhibit very little activity toward hydrogen peroxide direct synthesis (<0.1 mmol/L after 1 hour of reaction). On the other hand, significant hydrogen peroxide formation is observed in gold, palladium, and gold-palladium supported catalysts on activated carbon, indicating that the presence of metal active species is responsible for the activity. Table 2 lists the various catalysts that were created along with their chemical names and physical characteristics.

Using AuPd catalysts, Figure 1a compares the change in hydrogen peroxide concentration over time during the reaction. As can be seen, nitric acid pre-treatment of the support appears to be essential for achieving high productivities because it stops hydrogen peroxide from decomposing over extended reaction times. After 10 minutes of reaction, this effect becomes evident, as the productivity of the AuPd catalyst supported on acid-treated carbons (AP20 and APO20) increases while the concentration of H₂O₂ formed by the catalyst decreases on untreated carbon. Accordingly, the concentration of the untreated bimetallic catalyst is 11 mmol/L after 10 minutes, and it has dropped by about 50% to 5.6 mmol/L after 90 minutes.

Likewise, after 10 minutes, the concentration of the APO catalyst was 18 mmol/L, and after 90 minutes, it dropped to 11 mmol/L. After 90 minutes, the concentrations rose to 19 and 36 mmol/L, respectively, in comparison to AP20 and APO20's concentrations of 13 and 27 mmol/L after 10 minutes.[10] The industry's ability to remain viable depends on the decrease in hydrogen peroxide concentration, which is unquestionably directly related to the process's hydrogen selection. The APO20 catalyst exhibits a hydrogen selectivity of >99%, whereas the AP20 counter catalyst has a hydrogen selectivity of only 89%. According to earlier research, acid pretreatment can encourage the creation of bimetallic particles that are rich in gold, which prevents O-O bond cleavage during the dissociation reaction.[11] Carbon-containing metals have surface areas between 800 and 1000 m²g⁻¹, which are smaller than those of carbon supports. Figure 2 displays the AuPd bimetallic catalysts' adsorption-desorption isotherms supported on ordered activated carbons. For comparison, the activated carbon supports' isotherms are also plotted. [12] Based on the IUPAC classification, all of the isotherms match up to a type IV isotherm, which has a hysteresis loop because of capillary condensation in the mesopores. For every sample, a consistent pore size distribution is obtained, which is in line with the reported properties of ordered CMK-3 materials. The mean pore size of the samples is approximately 3 nm. [13]

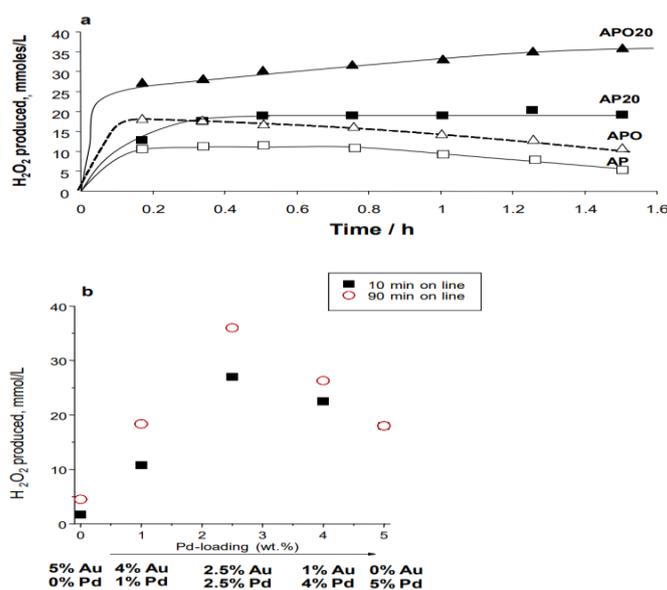


Figure 1. a) The direct synthesis of hydrogen peroxide from molecular oxygen and hydrogen: evolution of the H₂O₂ concentration with the time line for AuPd/carbon catalysts. b) The impact of the Au/Pd content in catalysts supported on ordered carbon that has been pre-treated on the productivity to H₂O₂ following 10 or 90 minutes on line. The text contains the reaction conditions.

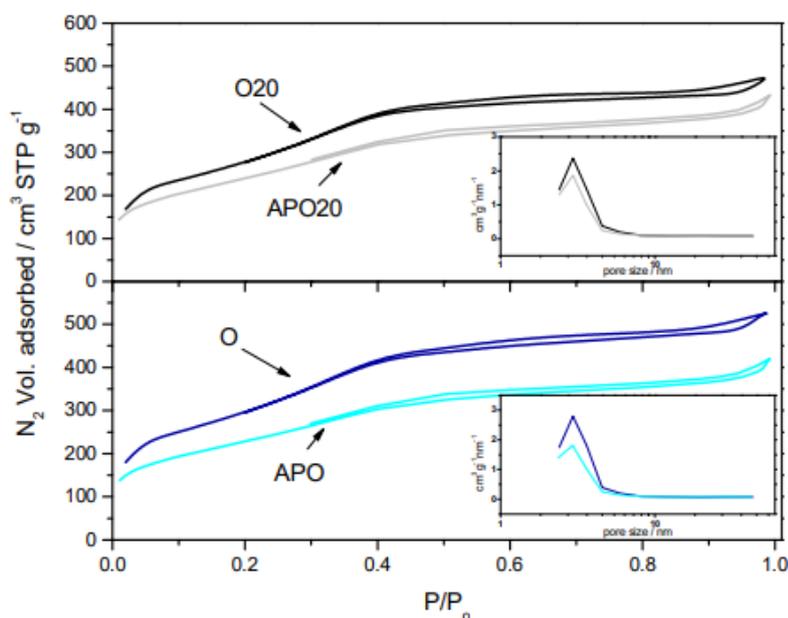


Figure 2. Adsorption–desorption isotherms for the ordered carbon supports and for the Au-Pd catalysts supported on ordered activated carbons.

Application of H₂O₂ as an in situ oxidant

Propylene epoxidation to propylene oxide: Use of H₂O₂ as an in situ oxidant in propylene epoxidation to produce propylene oxide. An important industrial chemistry raw material is propylene oxide (PO). Non-ionic surfactants, polyurethanes, resins, and other chemicals are mostly made with it. This is important in the petroleum, chemical, pesticide, and textile industries. The co-oxidation method and chlorohydrin method are the main industrial PO production methods [14], but the chlorohydrin method uses a lot of water and produces a lot of wastewater and waste. The co-oxidation method requires expensive equipment and a complicated process.[15] The new hydrogen peroxide direct oxidation method (HPPO) epoxidizes propylene to PO using H₂O₂. Production yields only propylene oxide and water. Thus, the process is simple, yields well, and is pollution-free, providing environmental and economic benefits (Fig. 3 a).

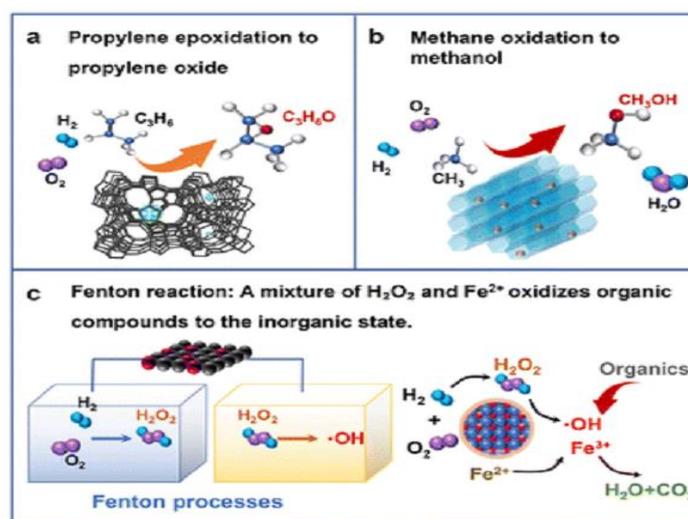


Fig. 3 Schematic diagram of (a) propylene epoxidation to epoxypropene, (c) Fenton reaction, and (b) methane oxidation to methanol.

Current industrial HPPO uses H_2O_2 solution and propylene (C_3H_6) gas as raw materials and a titanium–silicon catalyst to oxidize in water or methanol. H_2O_2 production must be near to avoid transportation costs. Thus, exploring in situ propylene oxidation with H_2O_2 as a feedstock and H_2 , O_2 , and C_3H_6 has economic, environmental, and future benefits. According to reports, TS-1, Ti-MCM-41, and their oxide supports [31–33] loaded with precious metals like Pd, Au, Pt, or their combinations form a bifunctional catalyst.

Catalytic selectivity to propylene oxide remains a problem. Chen et al. found that 0.2% Pd/TS-1 and 0.02 Pt%/TS-1 catalysts in compressed carbon dioxide mediums increase PO selectivity to 81.8% with ammonium acetate as the inhibitor.[34] Additionally, adding inorganic salts like Cs_2CO_3 , [35], CsNO_3 , [36], and CsCl [37] to the reaction system could inhibit propylene hydrogenation, PO hydrolysis, and PO with methanol and increase PO yield. The goal of future research is high PO selectivity without a promoter.

Fenton reaction

The Fenton reaction involves passing organic pollutants through a mixed solution of H_2O_2 and Fe^{2+} , which disproportionates to produce hydroxyl radicals and other strong oxidizers (Fig. 3 b). Chemical methods oxidize and decompose organic matter under mild conditions. It is a promising advanced catalytic oxidation technology for organic pollutant degradation in low-to-medium wastewater.

Esplugas et al. compared ozone, ultraviolet light, H_2O_2 , Fe^{2+} , and photocatalysis on phenol oxidative degradation. [38] The Fenton reagent degraded phenol fastest. Environmentally friendly oxygen and water were the only oxidation products of H_2O_2 . Simple operation, non-toxicity, fast reaction, and complete degradation characterized this process. The anthraquinone method produces high-concentration H_2O_2 commercially, which is expensive to transport and dilute. Thus, exploring direct in situ H_2O_2 generation for Fenton wastewater treatment is crucial and beneficial. For DSHP, Osegueda et al. created a membrane catalytic reactor with Pd as the active species. The reaction system showed good phenol oxidation activity after Fe^{2+} was added. Thus, in situ H_2O_2 generation directly used Fenton reaction feasibility. A loaded Pd–Fe bimetallic catalyst was more effective and active than commercial H_2O_2 for in situ phenol degradation, according to Underhill et al. [40] However, phenol oxidation intermediates have reduced the active ingredient Fe's stability and longevity. Future studies can optimize the catalyst or reaction system to increase catalyst life and stability, maintaining phenol degradation activity.

Methane-to-methanol oxidation

Methane is abundant and widespread. The selective conversion of methane molecules into liquid fuels and other chemicals makes natural gas use efficient. This helps restructure energy sources and produce green chemicals. The direct partial oxidation of methane to methanol is always difficult. The industrial conversion of methane to methanol has harsh production conditions and high process requirements. Selectivity can be achieved, but it is expensive and polluting, which hinders green chemical production.

Thus, researching new and environmentally friendly green oxidants like H_2O_2 to replace concentrated sulfuric acid or O_2 to selectively oxidize methane to produce methanol under mild reaction conditions is important economically and environmentally (Fig. 3 b). Rahim et al. proposed that the supported Au–Pd/ TiO_2 bimetallic catalyst provided good DSHP catalytic performance without a promoter. [41] Rahim et al. used it for in situ methane oxidation to methanol [42]. In situ H_2O_2 synthesis was better at capturing O_2 and generating reactive oxygen species in the liquid phase than commercial H_2O_2 . Thus, in situ methane-to-methanol oxidation may be efficient. Jin et al. hydrophobically treated silicate molecular sieves with organosilanes to encapsulate Pd–Au alloy nanoparticles. [43] H_2O_2 formed in zeolite crystals by mass transfer of H_2 and O_2 . The hydrophobic groups in the outer layer of zeolite may prevent H_2O_2 diffusion and increase its concentration. Methane molecules can now enter the zeolite interior through the hydrophobic layer and react with H_2O_2 . This method enhanced reaction efficiency, yielding $91.6 \text{ mmol h}^{-1} \text{ g}^{-1}$ methanol.

The yield of methanol from oxidized methane is still low and far below what is needed for industrial applications, but research is progressing. Thus, designing and developing highly active catalysts or improving reactors and process routes to increase methanol yields remains a major challenge for future research.

4. Conclusions

Ordered mesoporous carbons with a CMK-3 structure and acid treatment support highly dispersed bimetallic gold-palladium nanoparticles between 2 and 3 nanometers better than non-ordered carbons. This is because the former involved alloy nanoparticle encapsulation with the latter. Acid pre-treatment of both supports improves metal dispersion and gold enrichment of smaller nanoparticles. DSHP produces H_2O_2 cheaply and sustainably. Industrialization requires Pd catalyst optimization. Selectivity, activity, and cost must improve. In situ H_2O_2 oxidation reactions like propylene epoxidation, Fenton reaction, and methane oxidation to methanol are mild, eco-

friendly, and cost-effective. Research on in situ oxidation systems using H₂, O₂, and organic materials is important for chemical market and safety production.

5. References

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