

SYNTHESIS OF HYDROGEN PEROXIDE

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Chemistry 671

Introduction

- **Oxidation**

- Functionalize molecules (selective or partial oxidation)
- Remove pollutant (complete oxidation)

- **Oxidizing Agents**

- Oxygen gas
- Other oxidants (Sodium perborate, metallic peroxide etc.)
- **Hydrogen peroxide**

- **Problems with oxygen gas**

- Triplet ground state(in oxygen)
- Organic substrate (singlet ground state)

- **Problems with other oxidants**

- Separation, poor atom efficiency, polluting

- **Hydrogen peroxide**



Demand for hydrogen peroxide

- **Current market of H₂O₂**

- Three million metric tons per year
- As bleaching agent
- As cosmetics, disinfectants
- Chemical synthesis

- **In synthetic process**

- Propylene oxide (PO)
 - polyurethanes
- Annual Production of PO is >six million metric tons
- Market of PO is increasing by 4-5% per year
- Presently PO is produced by oxidation of propene by organic peroxide



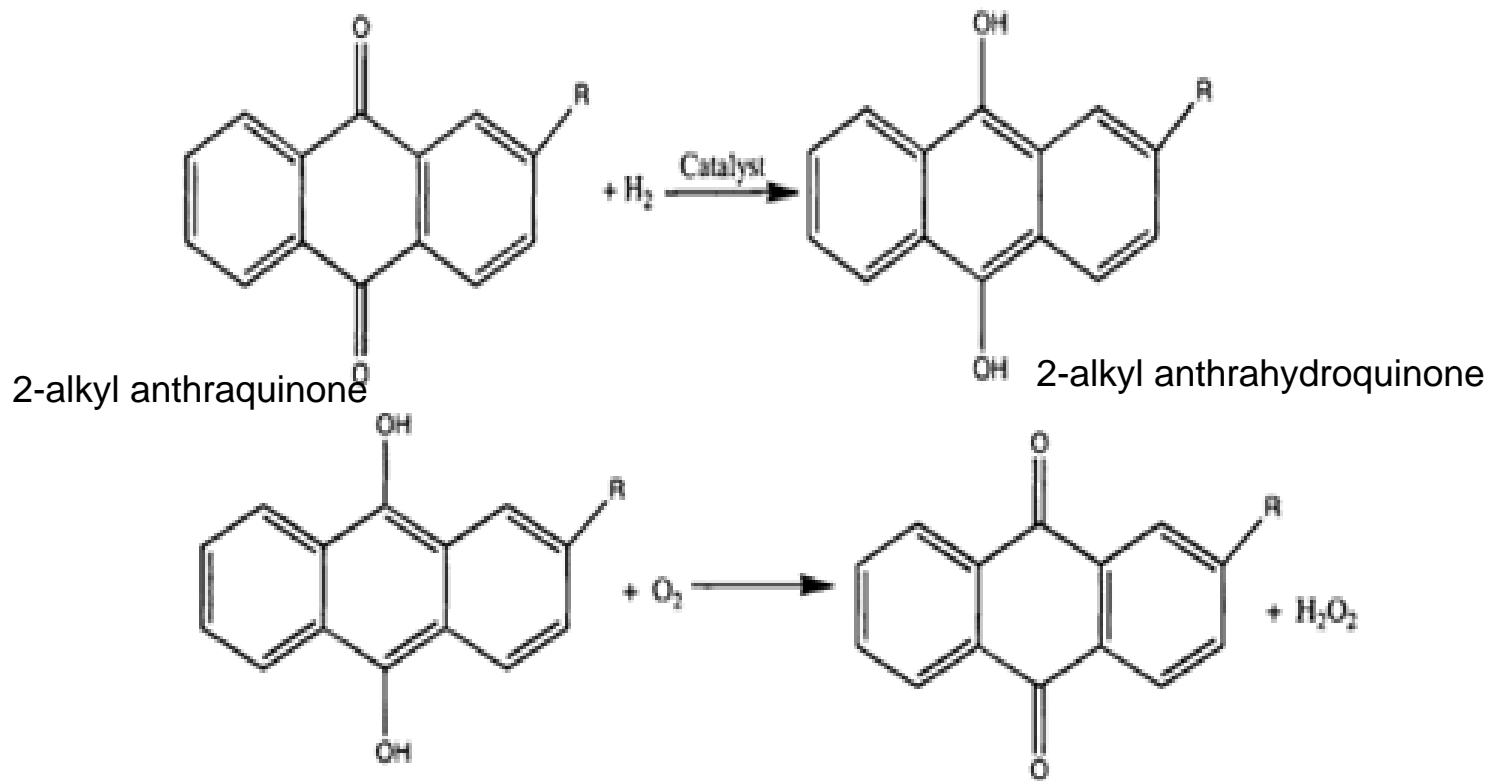
- Major PO producing company are designing a plant that produces 250,000 Metric tons/year of PO

- Needs 180,000 Metric tons of H₂O₂

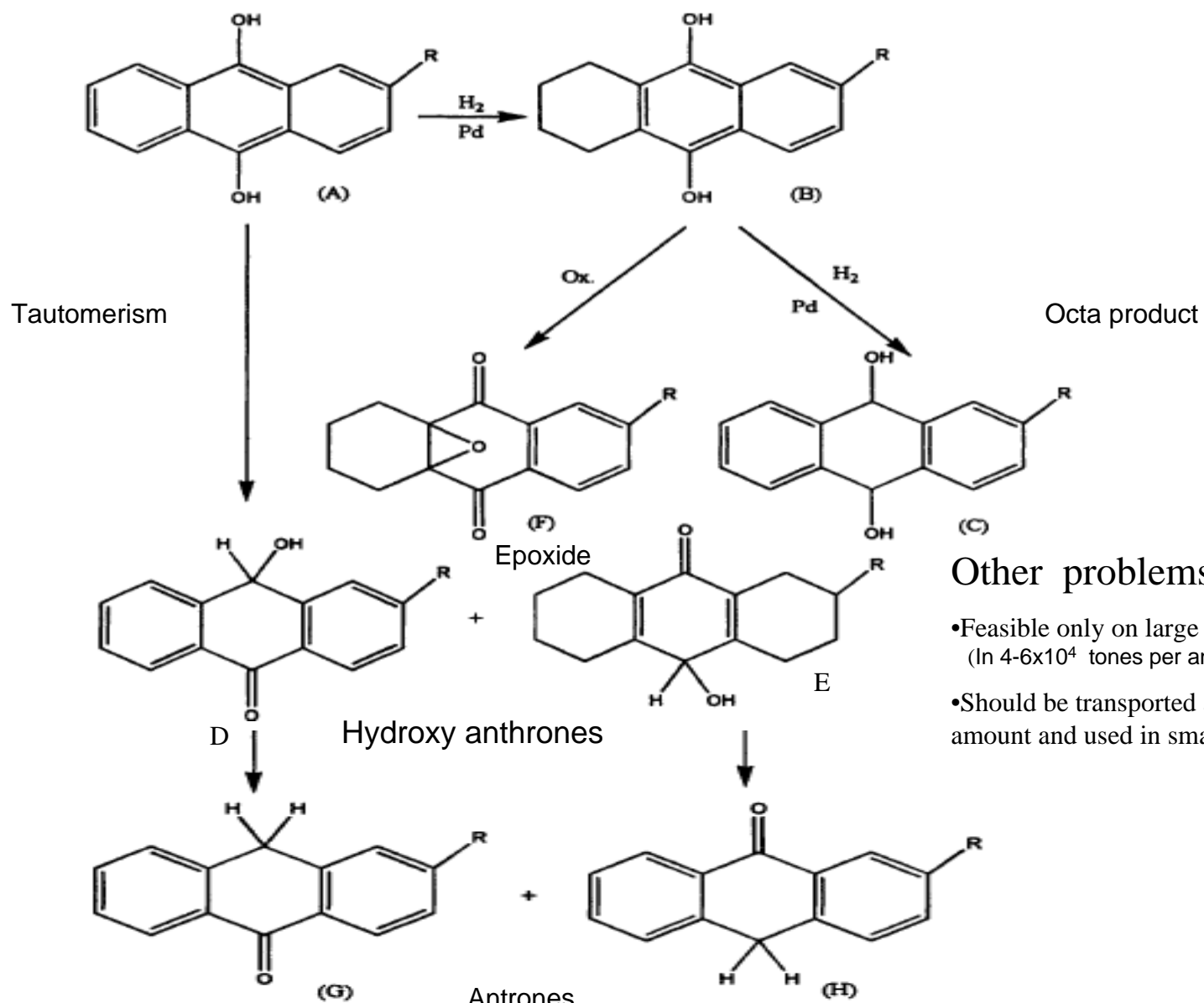
<http://www.degussa.com/>

Synthesis

- Is synthesis process **green**?



Synthesis of hydrogen peroxide from Anthraquinone



Other problems:

- Feasible only on large scale production (In $4-6 \times 10^4$ tones per annum)
- Should be transported and stored in large amount and used in small amount

Secondary reactions taking place in the presence of 2-alkylanthrahydroquinones.

- Direct synthesis

Two reasons

- 1.Green
- 2.Small scale production

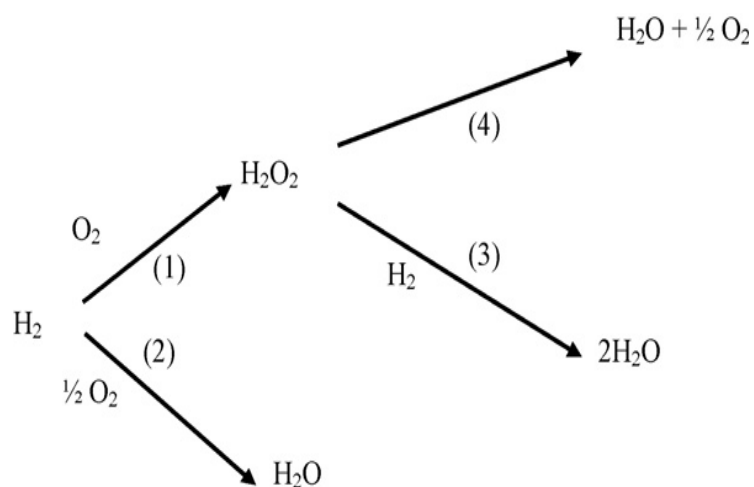


Hydrogen and oxygen both are environmentally friendly reagents/No waste/very cost effective

Historical overview of direct synthesis

- Dr.Hugo Henkel and Dr. Walter Weber June 16 ,1913 filed a patent for direct combination of H_2 and O_2 to give H_2O_2
- Process claimed:
 - Porous pipe is impregnated with catalyst (**Pd**, Pt or Ni)
 - The pipe is placed under the water in a vessel under excessive pressure of oxygen (so the oxygen is in contact with out side of the pipe)
 - In to the interior of the pipe ,gaseous H_2 is forced ,the reaction occurs and hydrogen peroxide is produced.
- Pospelova,Kobozev,Eremin(1961)
 - Pd black,0.001N KCN,0.1 N H_2SO_4 ,20% H_2 – initial yield 80 %

Problems with direct hydrogen peroxide synthesis



Which one is major route between these two?

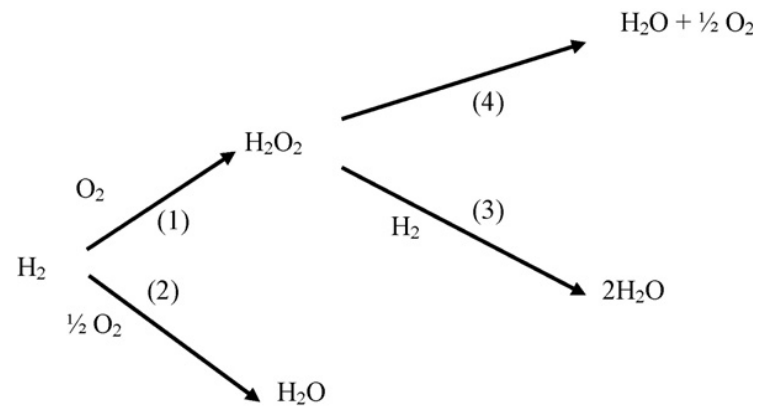
The main problems with direct synthesis

- H_2/O_2 mixture is explosive
- Direct catalytic combination of H_2 with O_2 prefers to give H_2O rather than H_2O_2 (selectivity)
- The catalyst active for production of H_2O_2 facilitates its decomposition

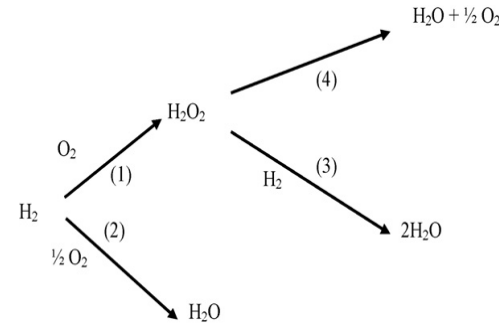
Fig. Various reactions during direct synthesis of hydrogen peroxide

- The favorable conditions
 - Lower temperature
 - Short reaction time
 - High pressure
 - Additive

- **Catalyst**



- Catalysts
Au, Ag, Pd, Au-Pd, Pd-Pt,
- Promoters
 - Acids
 - Bromide ions (NaBr)
- Role of acids
 - H_2O_2 is more stable in acidic condition. When $[\text{H}^+]$ is sufficient in the reaction medium, rxn 3 is suppressed
- Role of bromide ions
 - Small amount of bromide improves selectivity of H_2O_2
 - More bromide reduces the concentration of H_2O_2 severely
- Reasons: Br^- is poison for Pd catalyst
 - Block very active water producing sites
(Poison the catalytic sites active in breaking O-O bond)
 - At more concentration it destroys the catalyst

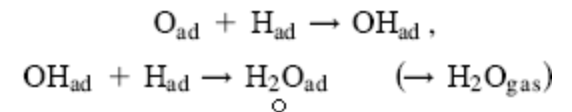
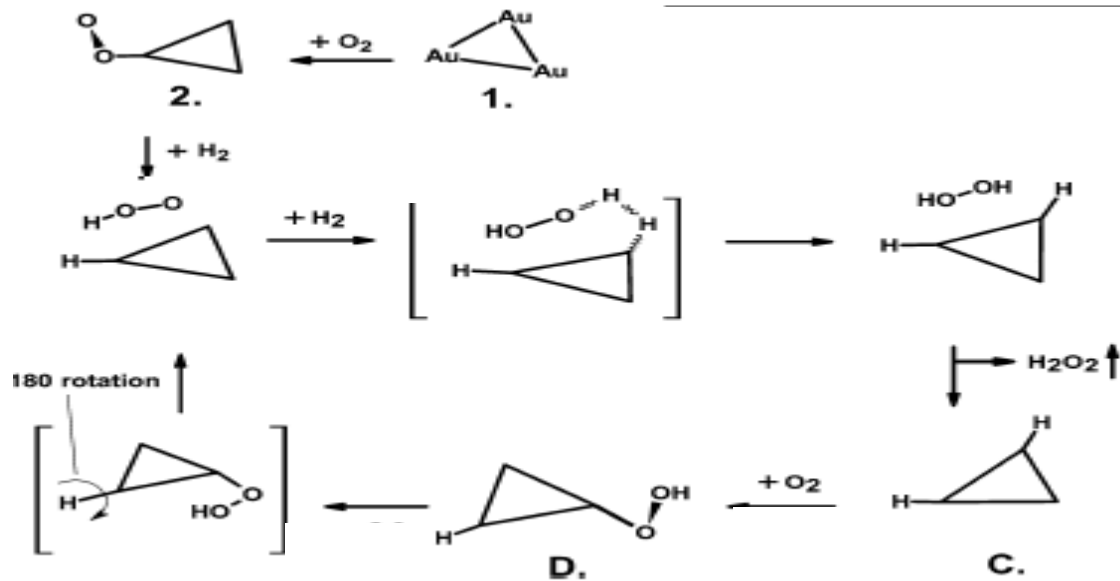


Mechanisms of synthesis of hydrogen peroxide

Table 2
Elementary steps involved in the reaction of hydrogen and oxygen on noble metal surfaces

Adsorption	(1) $\text{H}_2(\text{gas}) \rightarrow \text{H}_2$ (2) $\text{O}_2(\text{gas}) \rightarrow \text{O}_2$
Dissociation	(3) $\text{H}_2 \rightarrow 2 \text{H}$ (4) $\text{O}_2 \rightarrow 2 \text{O}$
Radical formation	(5) $\text{O}_2 + \text{H} \rightarrow \text{OOH}$ (6) $\text{O} + \text{H} \rightarrow \text{OH}$ (7) $\text{O}_2 + \text{H} \rightarrow \text{O} + \text{OH}$ (8) $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$
OOH reactions	(9) $\text{OOH} + \text{H} \rightarrow \text{H}_2\text{O}_2$ (10) $\text{OOH} + \text{H}_2 \rightarrow \text{H}_2\text{O}_2 + \text{H}$ (11) $\text{OOH} + \text{H} \rightarrow 2 \text{OH}$ (12) $\text{OOH} \rightarrow \text{O} + \text{OH}$
OH reactions	(13) $\text{OH} + \text{H} \rightarrow \text{H}_2\text{O}$ (14) $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ (15) $2 \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$ (16) $2 \text{OH} \rightarrow \text{H}_2\text{O}_2$ (17) $\text{OH} + \text{O}_2 \rightarrow \text{OOH} + \text{O}$ (18) $\text{OH} + \text{OOH} \rightarrow \text{H}_2\text{O}_2 + \text{O}$
Desorption	(19) $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O}_2(\text{gas})$ (20) $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}(\text{gas})$

Fig. Reactions involved in H_2O_2 production



Mechanism of formation of water

Mechanism of formation of H_2O_2

Definitions

- Conversion=(moles hydrogen consumed/moles hydrogen fed)x100%
 - Selectivity= $\frac{[H_2O_2]}{[H_2O_2] + [H_2O]} \times 100\%$
=moles of H_2O_2 produced/moles of hydrogen consumedX100%
 - Yield=Moles H_2O_2 produced/moles H_2 fedx100
 - Productivity =grams of H_2O_2 produced /grams Pd /pt xhr
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- The concentration of H_2O_2 is determined by iodometric titration/or titration with cerium sulfate or potassium permanganate
 - The concentration of H_2O is determined by Karl-Fischer titration method

Solvent system used

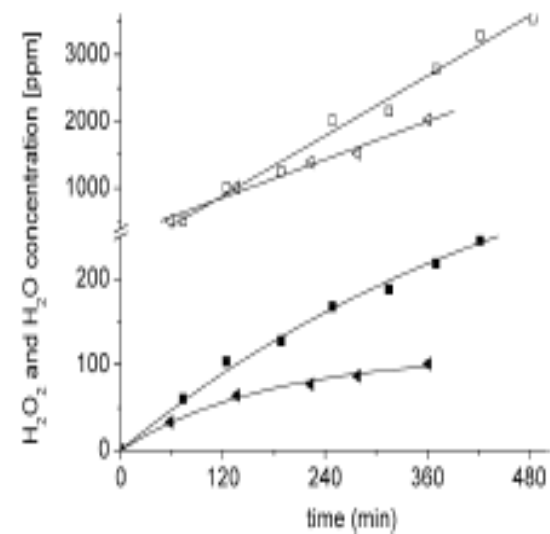
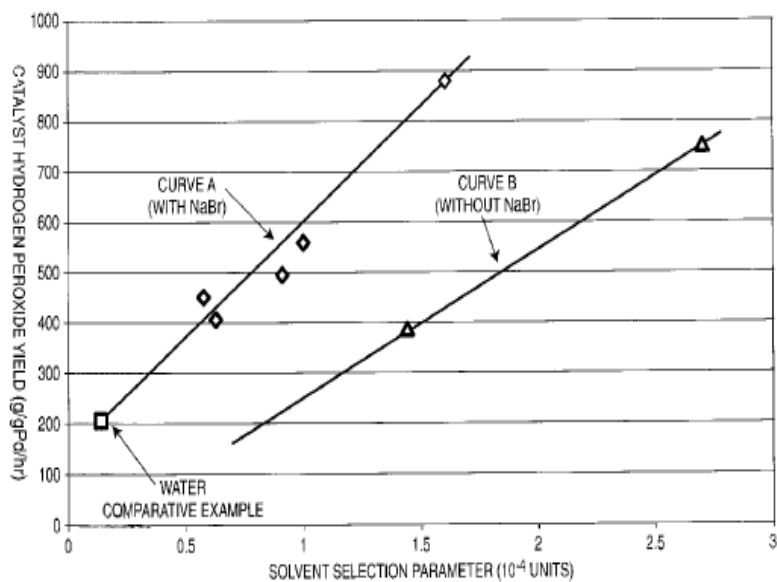
- Methanol is better than water
- Solvent selection parameter (SSP)

- Solvent selection

- Solvent selection parameter (ssp) = $\sum (w_i \times s_i)$
- w_i = weight fraction of solvent component i in liquid reaction mixture
- s_i = solubility of H_2 in pure component i expressed in mole fraction at 25 °C and 1 atm

- As ssp increases H_2O_2 production increases
- Should have one phase, yield is high
- NaBr 3ppm to 200 ppm by wt of liq.rxn medium.

Effect of Solvent and Br⁻



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Fig. 6. Effect of the Br⁻ concentration on the catalytic activity of TCM2. Squares, 6 ppm Br⁻; triangles, 60 ppm Br⁻ (filled symbols, H₂O₂ concentration; open symbols, H₂O concentration).

1. Solvent selection parameter VS. Hydrogen peroxide yield

1. United States Patent 6576214

2. S. Melada et al. / Journal of Catalysis 237 (2006) 213–219

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Effect of Liquid Solvent on Hydrogen Peroxide Synthesis

Example Number	Liquid Mixture	Catalyst to liquid ratio	H ₂ Solubility in Solvent	H ₂ Solubility in Water	Weight fraction solvent	Solvent Selection Parameter	H ₂ in Feed (vol. %)	H ₂ Conversion (%)	H ₂ O ₂ Concentration (wt %)	H ₂ O ₂ Yield (g/gPd/h)
			1 atm 25 C. 10 ⁻⁴ mole fraction	1 atm 25 C. 10 ⁻⁴ mole fraction		Average H ₂ Solubility 10 ⁻⁴ units				
<u>Comparative Example</u>										
1	Water	1/100		0.14	0	0.14	3	24.3	2.9	207
<u>Curve A Examples (with NaBr)</u>										
2	Methanol/Water	1/300	1.6	0.14	0.3	0.578	3	22	2.1	450
3	Acetonitrile/Water	1/300	1.76	0.14	0.3	0.626	3	18.9	1.9	407
4	Isopropanol/Water	1/300	2.7	0.14	0.3	0.908	3	19.8	2.3	493
5	Acetone/Water	1/300	3	0.14	0.3	0.998	3	61.1	2.6	557
6	Methanol	1/300	1.6	0.14	1	1.6	3	85.2	4.1	879
<u>Curve B Examples (without NaBr)</u>										
7	DMF	1/300	1.44	0.14	1	1.44	3	64.4	1.8	385
8	Isopropanol	1/300	2.7	0.14	1	2.7	3	82.4	3.5	750
<u>Other Examples</u>										
9	Hexane/Water *	1/300	6.6	0.14	0.3	2.078	3	79	0	0
10	Formaldehyde/Water	1/300	?	0.14	0.3	?	3	11.8	0.3	64

Effect of solvent in production of hydrogen peroxide

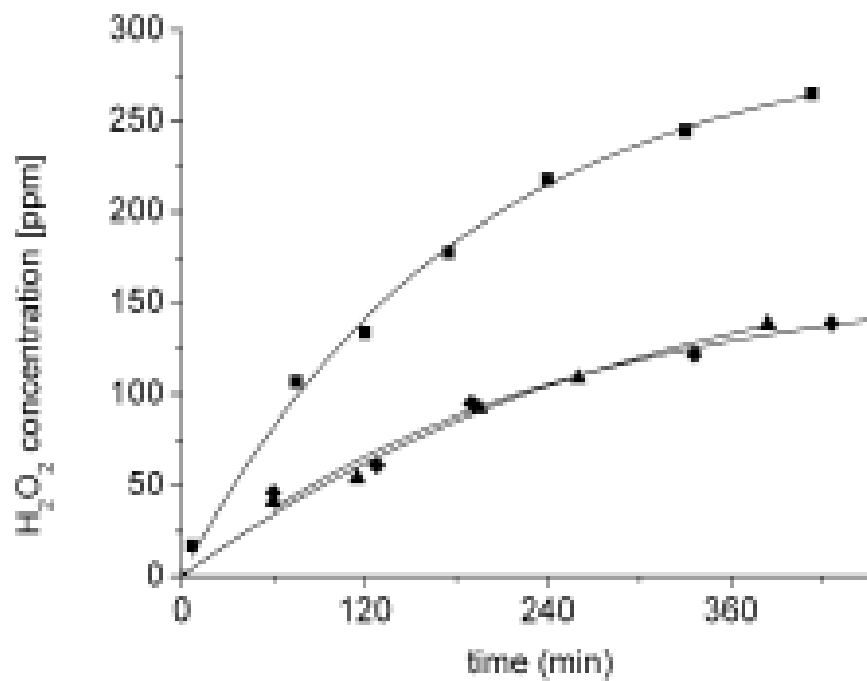


Fig. 3. H₂O₂ concentration profiles in different reaction media for TCM1.
■, 100% methanol; ◆, 100% water; ▲, 50% water and 50% methanol.

- The usefulness of solvent other than water
 - Most oxidation process involving H_2O_2 are carried out in organic solvent
 - Hydrogen and oxygen solubilities are higher in organic solvent than in water
 - Dry organic media helps to measure the produced water and measure the catalytic activity and selectivity.

Effect of catalyst mass and reaction time for the formation of H₂O₂

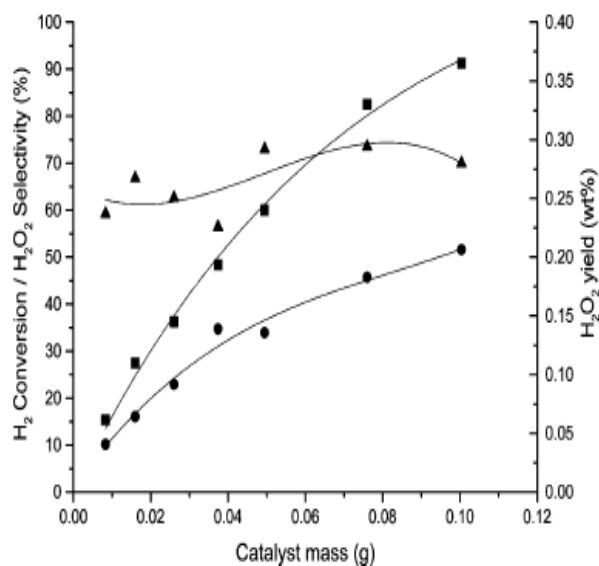


Fig. 2 Effect of catalyst mass on production of H₂O₂ using 0.6 wt.% Pd/sulfonated carbon, ● = H₂ conversion, ▲ = H₂O₂ selectivity, ■ = H₂O₂ yield.

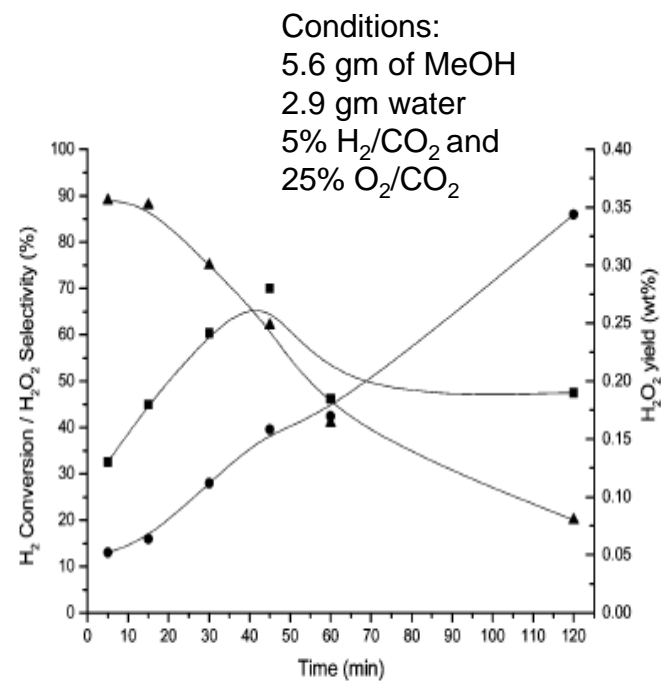


Fig. 3 Progress as a function of time of the reaction between H₂ and O₂ using 0.6 wt.% Pd/sulfonated carbon, ● = H₂ conversion, ▲ = H₂O₂ selectivity, ■ = H₂O₂ yield.

London Philip et.al. Direct synthesis of hydrogen peroxide from H₂ and O₂ using Pd and Au catalysts, *Phys. Chem. Chem. Phys.*, 2003, 5, 1917–1923

Effect of temperature on hydrogen peroxide production

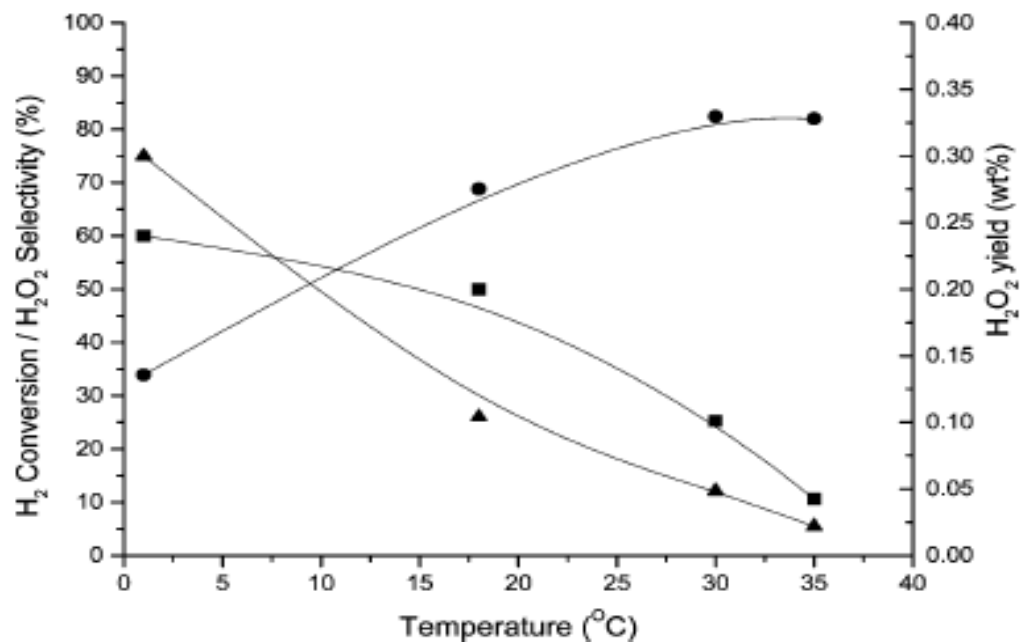


Fig. 4 Influence of temperature on H₂O₂ production using 0.6 wt.% Pd/sulfonated carbon ● = H₂ conversion, ▲ = H₂O₂ selectivity, ■ = H₂O₂ yield.

Bimetallic catalyst

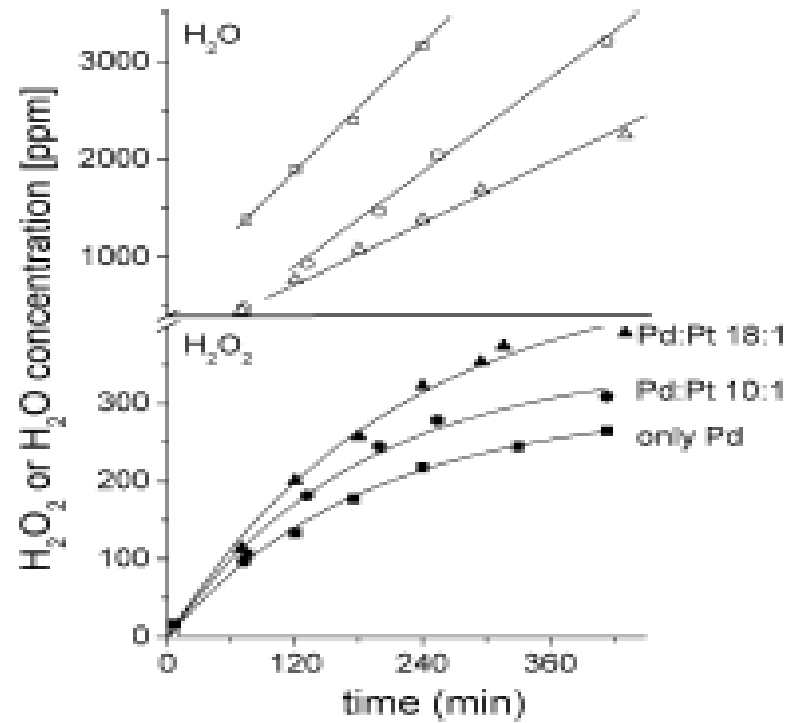


Fig. 7. Catalytic performance of bimetallic samples (TCM3 and TCM4) compared to a monometallic sample (TCM1). Filled symbols, H₂O₂ concentration open symbols, H₂O concentration.

Studies on possible decomposition route of hydrogen peroxide

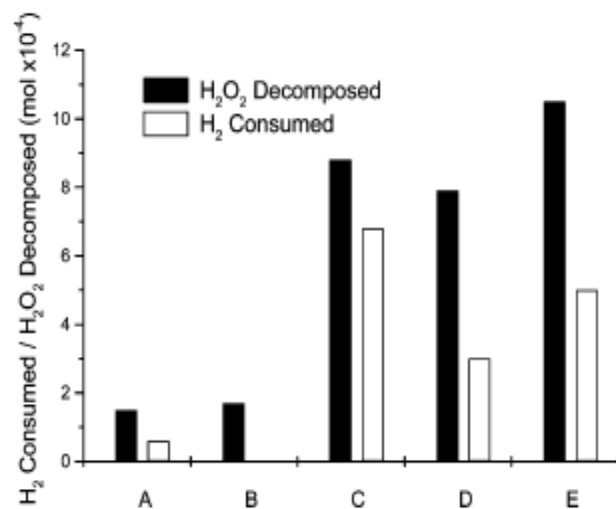
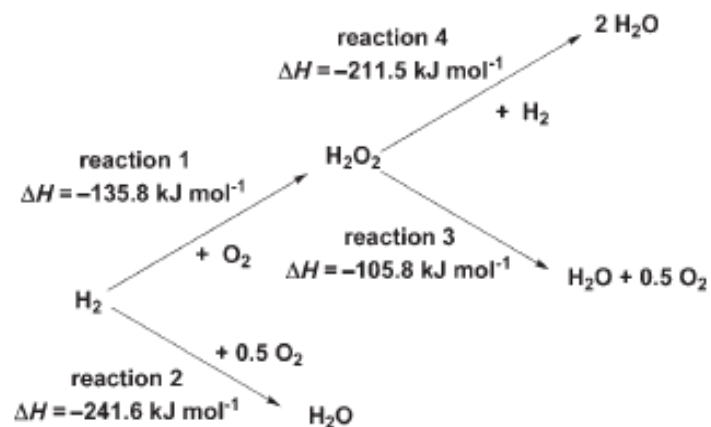
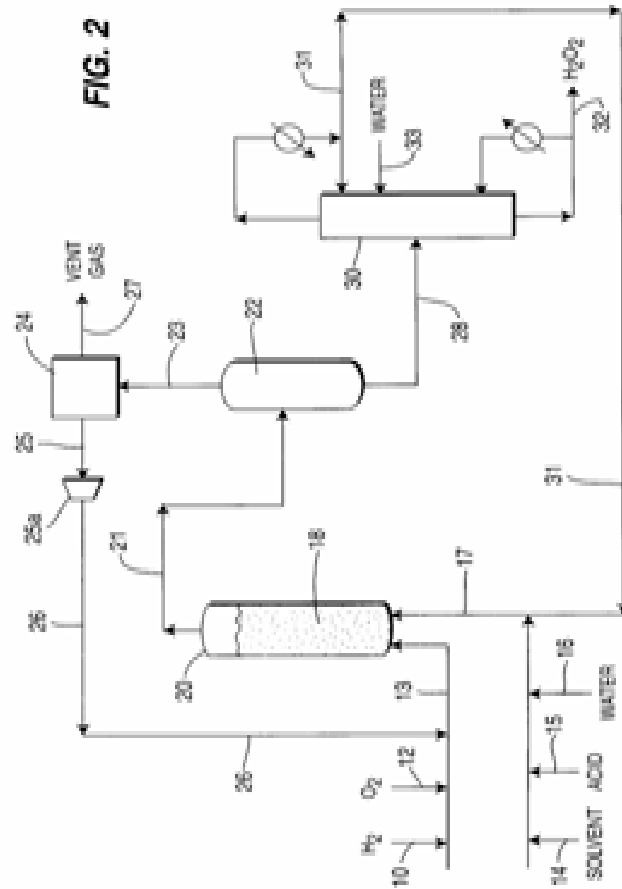


Fig. 6 Decomposition of H₂O₂ under different experimental conditions using 0.6 wt.% Pd/sulfonated carbon, (A) = no catalyst, H₂, 1°C, (B) = catalyst, O₂, 1°C, (C) = catalyst, H₂, 1°C, (D) = catalyst, H₂, HBr (1.8 × 10⁻⁵ mol l⁻¹), 1°C, (E) = catalyst, H₂, HBr (1.8 × 10⁻⁵ mol l⁻¹), 17°C, 3.7 MPa.

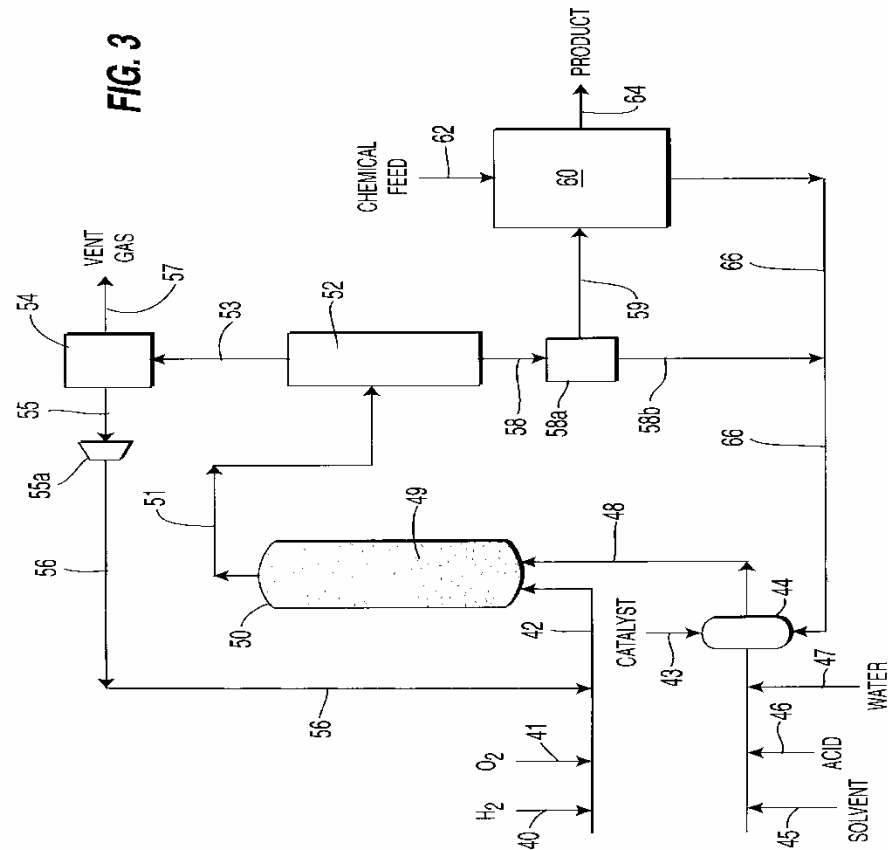




Direct synthesis of hydrogen peroxide

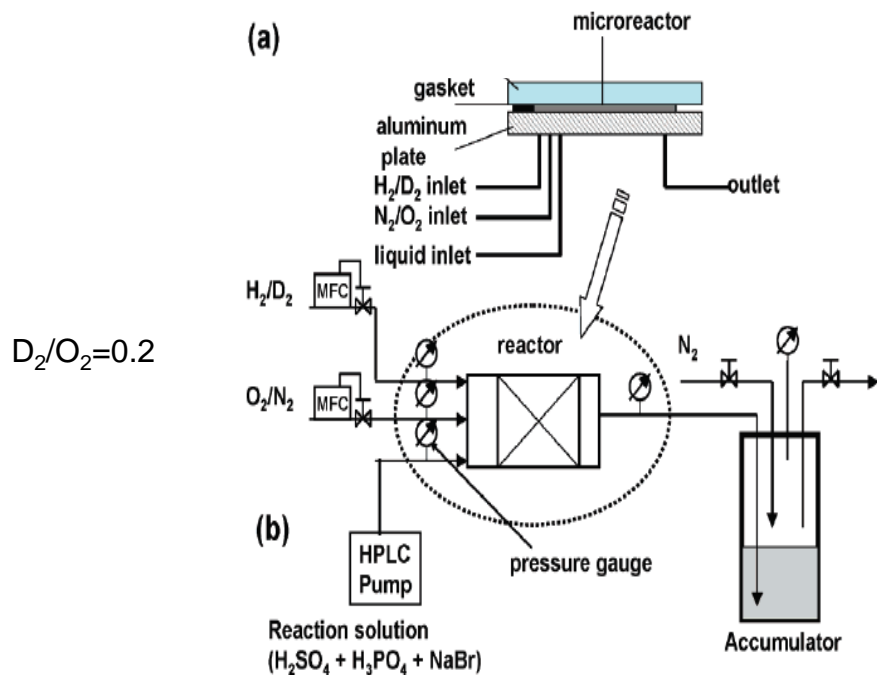
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United States Patent 6576214



Direct synthesis of Hydrogen peroxide combined with organic synthesis

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re 3. Hydrogen peroxide synthesis setup: (a) microreactor setup and (b) total system for direct synthesis of hydrogen peroxide.

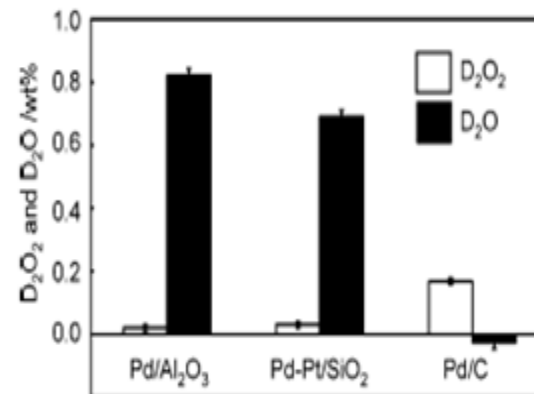


Figure 6. Comparison of formation of peroxide (open box) and water (filled box) on different catalyst supports, Pd/Al_2O_3 (13.5 mg), $Pd-Pt/SiO_2$ (29.0 mg), and Pd/C (15.6 mg). Conditions were as follows: deuterium flow rate 1.0 sccm, oxygen flow rate 4.0 sccm, and liquid (reaction solution flow rate 0.1 mL min^{-1} .

$T=293K, P=2 MPa, 0.05N H_2SO_4, H_3PO_4=0.015N, NaBr=5.1 \times 10^{-4} mol L^{-1}$

SCCM=standard cubic centimeter per minute

H_2O_2 produced
=0.2 wt%

D_2 conversion =3 %

Selectivity is nearly 100 %

Rate of production -first order in
hydrogen partial pressure

Conclusions:

- Direct synthesis of H_2O_2 from hydrogen and oxygen is convenient than anthraquinone process
- Pd/gold or Pd/Pt catalyst is better than single metal
- Short reaction time, high pressure and low temperature are favorable conditions
- There is possibility of making portable hydrogen peroxide synthesis device for small scale production
- Methanol/water mixture is good solvent system, NaBr is good additive and presence of acid are necessary conditions for maximizing the selectivity of hydrogen peroxide synthesis

References

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