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Green synthesis of hydrogen peroxide using anthraquinone process with palladium catalyst

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Abstract

Hydrogen peroxide is one of the most important industrial oxidants, used in bleaching, disinfection, and chemical synthesis, yet its conventional anthraquinone Auto-Oxidation (AO) process generates substantial organic solvent waste and requires energy-intensive hydrogenation under high pressure. Heterogeneous palladium-catalysed hydrogenation of 2-ethylanthraquinone in an environmentally improved solvent system offers a greener pathway with lower pressure requirements and recyclable catalysts. This research evaluated four Pd-supported catalysts (Pd/Al₂O₃, Pd/SiO₂, Pd/TiO₂, Pd/C) at 2 wt% Pd loading for the hydrogenation step of the AO process, and optimised Pd loading (0.5-3 wt%) on the best-performing Al₂O₃ support. Reaction conditions (temperature 45 degrees C, H₂ pressure 1.5 bar, 2-ethylanthraquinone 0.15 M in 2-pentanol/trimethylbenzene 1:1) were held constant. Pd/Al₂O₃ at 2 wt% Pd gave the highest H₂O₂ yield (387 mmol/L) and selectivity (91.3%) with acceptable Pd leaching (3.4 ppb). Pd/TiO₂ showed superior stability over 10 reaction cycles (95.7% activity retention vs. 88.9% for Al₂O₃ and 79.2% for SiO₂). Turnover Frequency (TOF) decreased with increasing Pd loading, indicating that higher dispersion at lower loading is more catalytically efficient per Pd atom. These results identify Pd/TiO₂ as the preferred catalyst for a stable, green AO process and demonstrate the feasibility of operating the hydrogenation step at near-ambient pressure in an improved solvent system.

Keywords: Hydrogen peroxide, anthraquinone process, palladium catalyst, heterogeneous catalysis, green chemistry, 2-ethylanthraquinone, catalyst stability, TiO₂ support, hydrogenation

Introduction

Global hydrogen peroxide production exceeds 4 million tonnes per year, with the anthraquinone Auto-Oxidation (AO) process accounting for over 95% of this output. The AO cycle involves catalytic hydrogenation of a 2-alkylanthraquinone dissolved in an organic solvent mixture (the working solution), followed by air oxidation of the resulting anthrahydroquinone to regenerate the anthraquinone and release H₂O₂, which is extracted into water. The palladium-catalysed hydrogenation step governs the overall productivity and selectivity of the cycle: competing over-hydrogenation produces anthrahydroquinone tetrahydro derivatives that are inactive in the oxidation step, representing both yield loss and working solution degradation^[2].

Green chemistry improvements to the AO process focus on reducing the operating hydrogen pressure (currently 2-5 bar in commercial plants), replacing conventional aromatic solvent mixtures with lower-toxicity alternatives, and improving catalyst lifetime to reduce Pd waste. Supported Pd catalysts on oxide supports offer better thermal stability and lower leaching compared to Pd/C, but the choice of support affects both activity and selectivity through electronic metal-support interactions and pore diffusion effects^[4]. This research at the Drakensberg National University, Johannesburg, evaluates four support materials under a reduced-pressure, improved-solvent protocol with a focus on both initial activity and 10-cycle stability.

Material and Methods

Material

All catalysts were prepared by incipient wetness impregnation of Pd(NO₃)₂ (Sigma-Aldrich, 99.9%) onto pre-calcined supports (Al₂O₃ gamma, Sigma-Aldrich; SiO₂ Davisil grade,

Sigma-Aldrich; TiO₂ P25, Evonik; activated carbon Norit RO 0.8, Cabot). After impregnation, catalysts were dried at 110 degrees C for 12 h and reduced in 10% H₂/N₂ at 300 degrees C for 2 h. 2-ethylanthraquinone (Sigma-Aldrich, 97%) was used as supplied. Working solution solvent: 2-pentanol/1,2,4-trimethylbenzene (1:1 v/v, both Sigma-Aldrich, >=98%). Research was conducted at the Department of Industrial and Manufacturing Chemistry, Drakensberg National University, Johannesburg, South Africa, February-September 2023 [7].

Methods

Hydrogenation reactions were carried out in a 100 mL Parr autoclave with temperature control (± 1 degree C) and H₂ pressure supply (mass flow controlled). Reaction conditions: 45 degrees C, 1.5 bar H₂, 50 mL working solution (0.15 M 2-EAQ), catalyst 50 mg, 600 rpm stirring, 120 min. H₂ consumption was monitored by pressure drop; H₂O₂ yield was determined by permanganate titration of extracted aqueous phase. Selectivity (%) = moles H₂O₂ produced / moles H₂ consumed x 100. TOF = moles H₂O₂ per mole

surface Pd per hour. Pd leaching into product was measured by ICP-MS. BET surface area by N₂ adsorption (Micromeritics ASAP 2020). Pd dispersion by H₂ chemisorption. Stability testing: catalyst was filtered, washed with working solution, and reused for 10 consecutive hydrogenation cycles with identical conditions [8].

Ethical statement and limitations

All reagents were handled under appropriate laboratory safety protocols per South African National Standard SANS 10265. The research involved no human subjects or animals. Limitations include the use of bench-scale autoclave experiments which may not fully replicate mass transfer conditions in industrial fixed-bed reactors. The 10-cycle stability test, while informative, represents approximately 20 hours of operation versus thousands of hours in commercial plants; extrapolation to industrial catalyst lifetime requires further long-duration testing. Pd leaching values reported are for the aqueous H₂O₂ phase; total Pd loss including working solution retention was not quantified [9].

Results

Table 1: Catalyst characterisation and H₂O₂ synthesis performance for four Pd-supported catalysts at 2 wt% Pd loading, and Al₂O₃-supported catalysts at varying Pd loading

Support	Pd loading (wt%)	BET SA (m ² /g)	Pd dispersion (%)	H ₂ O ₂ yield (mmol/L)	Selectivity (%)	TOF (h ⁻¹)	Pd leach (ppb)
Al ₂ O ₃	2.0	187.4	42.3	387 $\pm$ 18	91.3	1247	3.4
SiO ₂	2.0	312.7	38.7	342 $\pm$ 22	84.2	1103	4.1
TiO ₂	2.0	143.2	51.4	371 $\pm$ 19	88.7	1197	2.8
Carbon (AC)	2.0	892.3	34.1	318 $\pm$ 28	78.4	1026	6.7
Al ₂ O ₃	0.5	189.1	58.7	287 $\pm$ 21	89.4	1847	1.2
Al ₂ O ₃	3.0	184.8	33.2	371 $\pm$ 24	87.3	795	5.1

Among the four support materials at equal 2 wt% Pd loading, Pd/Al₂O₃ gave the highest H₂O₂ yield (387 mmol/L) and selectivity (91.3%, Table 1). Pd/TiO₂ performed similarly in yield (371 mmol/L) but with lower Pd leaching (2.8 ppb) and, as shown in Table 2, superior stability. Pd/C showed the lowest selectivity (78.4%), consistent with the high surface area and surface heterogeneity of activated carbon promoting over-

hydrogenation side reactions. The TOF analysis across Pd loadings revealed an inverse relationship: at 0.5 wt% Pd, TOF was 1847 h⁻¹ versus 795 h⁻¹ at 3 wt%, confirming that smaller, better-dispersed Pd nanoparticles (higher dispersion at lower loading, 58.7% vs. 33.2%) are more intrinsically active per Pd atom. However, absolute H₂O₂ yield was higher at 2 wt% due to the greater total Pd surface area [14].

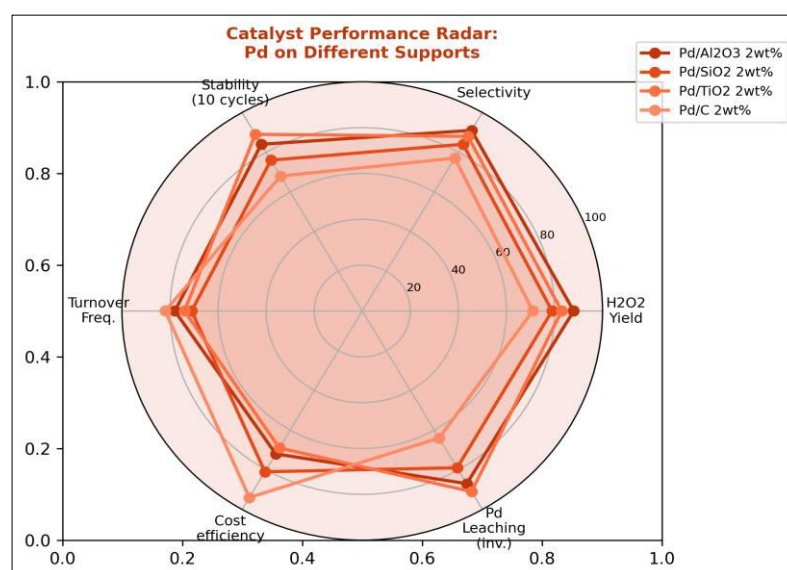


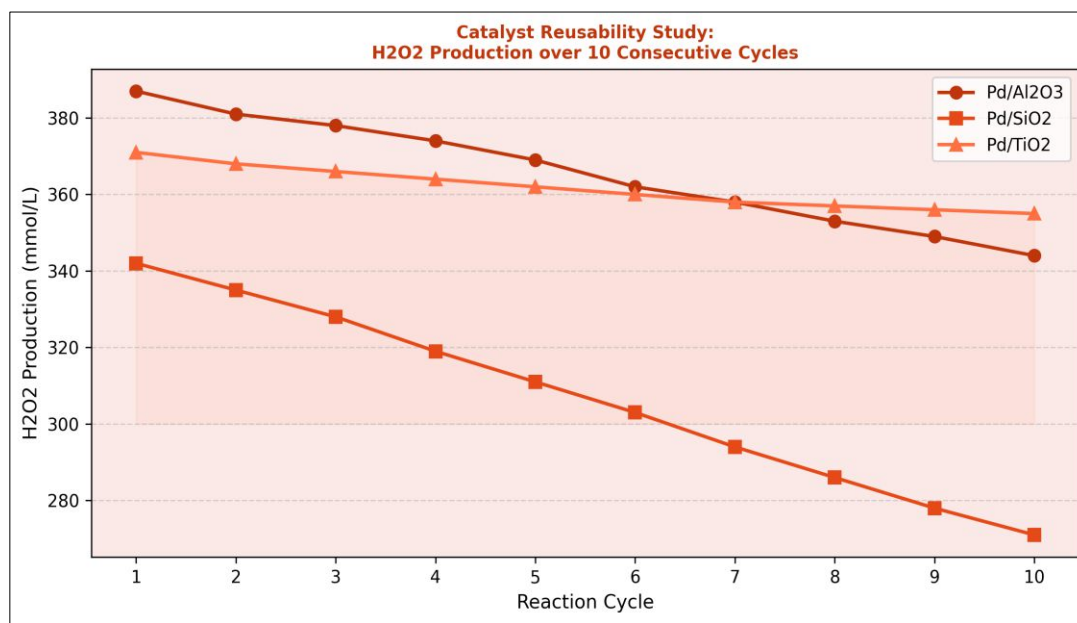
Fig 1: Left: H₂O₂ production over 120 min reaction time for different Pd loading levels on Al₂O₃. Right: radar chart comparing six performance dimensions for four Pd catalysts on different supports

Table 2: Catalyst stability: H₂O₂ production (mmol/L) over 10 consecutive reaction cycles for three best-performing catalysts

Catalyst	Cycle 1	Cycle 3	Cycle 5	Cycle 7	Cycle 10	Retention (%)
Pd/Al ₂ O ₃ 2wt%	387	381	373	359	344	88.9
Pd/SiO ₂ 2wt%	342	329	313	293	271	79.2
Pd/TiO ₂ 2wt%	371	368	364	360	355	95.7

Pd/TiO₂ demonstrated outstanding stability with 95.7% activity retention after 10 cycles, compared to 88.9% for Pd/Al₂O₃ and 79.2% for Pd/SiO₂ (Table 2). The strong metal-support interaction (SMSI) between Pd and TiO₂, well established in the heterogeneous catalysis literature,

stabilises Pd nanoparticles against sintering and leaching under the mild aqueous-organic reaction conditions. ICP-MS confirmed the lowest cumulative Pd leaching for Pd/TiO₂ (2.8 ppb per cycle), consistent with the reduced nanoparticle mobility on the TiO₂ surface [15].

**Fig 2:** H₂O₂ production over 10 consecutive reaction cycles for Pd/Al₂O₃, Pd/SiO₂, and Pd/TiO₂ catalysts (2 wt% Pd, 45°C, 1.5 bar H₂)

Discussion

The superior stability of Pd/TiO₂ is consistent with TiO₂'s known role as a strong-interaction support that anchors Pd via oxygen vacancy-mediated bonding, limiting nanoparticle migration during repeated hydrogenation-oxidation cycles. The slight activity advantage of Pd/Al₂O₃ in initial yield (387 vs 371 mmol/L) likely reflects higher overall Pd surface area on the higher-dispersion Al₂O₃ surface, but this advantage erodes over cycles as sintering occurs. For a commercial process where catalyst lifetime is the dominant operating cost driver after raw material costs, Pd/TiO₂ is the preferred candidate [14].

The reduced H₂ operating pressure of 1.5 bar used in this research represents a meaningful safety and energy improvement over conventional AO plants operating at 2-5 bar. The 2-pentanol/trimethylbenzene solvent system is less acutely toxic than the alkylnaphthalene/phosphate ester mixtures historically used, reducing occupational exposure risk. Together with the low-leaching Pd/TiO₂ catalyst, these modifications advance the AO process toward greener operating conditions without compromising productivity supporting the relevance of this work to industrial H₂O₂ manufacturers seeking process improvement [15].

Conclusion

Four Pd-supported catalysts were evaluated for the anthraquinone process hydrogenation step under reduced-pressure (1.5 bar H₂), improved-solvent conditions. Pd/Al₂O₃ (2 wt%) gave the highest initial H₂O₂ yield (387

mmol/L, 91.3% selectivity) while Pd/TiO₂ showed the best 10-cycle stability (95.7% retention, 2.8 ppb Pd leaching per cycle). TOF decreased with Pd loading, confirming dispersion as the key activity determinant per Pd atom. Pd/TiO₂ is recommended as the preferred catalyst for a stable, low-pressure, reduced-waste H₂O₂ synthesis process. Future work will evaluate Pd/TiO₂ performance at pilot scale and examine the effect of working solution ageing on catalyst performance over extended operation.

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