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The Direct Synthesis of Hydrogen Peroxide from H₂ and O₂ Using Pd-Ni/TiO₂ Catalysts.

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Summary.

The direct synthesis of hydrogen peroxide (H₂O₂) from molecular H₂ and O₂ offers an attractive solution to decentralised production compared to the anthraquinone process. Herein we evaluate the performance of a 0.5%Pd-4.5%Ni/TiO₂ catalyst in batch and flow reactor systems using water as a solvent at ambient temperature which makes synthesising high H₂O₂ concentrations challenging. Catalyst activity was observed to be stable to prolonged use in multiple batch experiments or in a flow system, with selectivities towards H₂O₂ of 97% and 85% respectively. This study was carried out in the absence of halide or acid additives that are typically used to inhibit sequential H₂O₂ degradation reactions showing that this Pd-Ni catalyst has potential to produce H₂O₂ selectively

Introduction.

The direct synthesis of hydrogen peroxide (H₂O₂) would offer an attractive alternative to the current anthraquinone oxidation (AO) process and potentially allow decentralised production. Accounting for more than 95 % of global H₂O₂ production the AO process is highly optimised. However there are concerns regarding the requirement for continuous replacement of the anthraquinone as a result of its over-hydrogenation and high energy requirements during the extraction and concentration of the formed H₂O₂. Furthermore, the AO process only proves to be economical on a large scale meaning that production has to be centralised. As a result H₂O₂ is often transported at high concentrations in the presence of acidic stabilisers, used to inhibit decomposition to H₂O. However, the use of such stabilizing agents often leads to decreased reactor lifetime and increased costs associated with their removal from product streams.

The direct synthesis of H₂O₂ from molecular H₂ and O₂ would offer an attractive alternative to the AO process, allowing for decentralized H₂O₂ production. The high activity of Pd-based catalysts for the direct synthesis reaction has been well known since 1914(1) and has received significant attention in the literature.(2-6) However, issues around selectivity have posed a major challenge to suppress H₂O₂ degradation pathways and can often only be achieved in the presence of acid or halide promoters(7-9). By comparison AuPd catalysts

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have been demonstrated to offer excellent selectivities towards H₂O₂ in the absence of stabilizing agents.(10-14) More recently we have reported that it is possible to replace Au with more abundant base-metals such as Sn, Ni, Zn and Co, which through exposure to successive calcination-reduction-calcination heat treatment can demonstrate selectivities towards H₂O₂ in excess of 95%. This has been attributed to the encapsulation of ultrasmall Pd-rich nanoparticles, responsible for H₂O₂ degradation by a secondary metal oxide.(15)

Subsequently further studies have reported enhanced catalytic performance can be achieved through the alloying of Pd with a range of secondary non- or semi-precious metals such as Ag,(16) Sb,(17) Te,(18) Sn(19), Ni(20) and Zn.(21) Enhancement in selectivity is often attributed to a reduction in the amount of extended Pd ensembles, resulting in a reduction in the rates of O-O bond scission, preventing the formation of H₂O from H₂O₂ decomposition or over hydrogenation.

In this work, we focus on the efficacy of our recently reported 4.5%Ni-0.5%Pd/TiO₂ catalyst.(15) In our previous study we highlighted the excellent selectivity towards H₂O₂ that can be achieved with this catalysts under conditions optimized for H₂O₂ production. Herein we demonstrate good catalytic performance under conditions less conducive towards H₂O₂ synthesis such as ambient reaction temperature and using water only as the reaction solvent in the absence of acid and halides (22). We further investigate the efficacy of the 4.5%Ni-0.5%Pd/TiO₂ catalyst in a flow regime, with the continual production of H₂O₂ highly desirable for industrial application.

Experimental.

Catalyst Preparation.

Bimetallic 5% PdNi/TiO₂ catalysts have been prepared on a wt. % basis by a conventional wet impregnation procedure, based on methodology previously reported in the literature.(15) The procedure to produce 0.5%Pd-4.5%Ni/TiO₂ (1 g) is outlined as follows. Aqueous solutions of Pd(NO₃)₂ (0.833 mL, 6 mg mL⁻¹, Johnson Matthey) and NiCl₂ (5 mL, 9 mg mL⁻¹, Sigma Aldrich) were combined with H₂O (HPLC grade), in a 50 mL round bottom flask, so that total volume was fixed to 16 mL. The resulting mixture was heated to 80°C in a thermostatically controlled oil bath with stirring (1000 rpm). Upon reaching 80°C TiO₂ (0.95 g, Degussa, P25) was added, the resulting slurry was then stirred continuously until a thick paste was formed. The paste was dried (110 °C, 16 h) and the resulting solid material was ground prior to calcination (500 °C, 3 h, 20 °Cmin⁻¹, static air). This was followed by reduction (200 °C, 2 h, 20 °C min⁻¹, 5 % H₂/ Ar) and re-calcined (400 °C, 3 h, 20 °Cmin⁻¹, static air).

Direct Synthesis of H₂O₂ using batch reactor conditions.

H₂O₂ synthesis was evaluated using a Parr Instruments stainless steel autoclave with a internal volume of 50 mL, equipped with a PTFE liner so that total volume is reduced to 33 mL, and a maximum working pressure of 140 bar. The autoclave liner was charged with catalyst (0.01 g) and solvent (8.5 g H₂O), then purged three times with 5% H₂/ CO₂ (0.7 MPa) before filling with 5 % H₂/ CO₂ to a gauge pressure of 29 bar, followed by the addition of 25 % O₂/ CO₂ (11 bar). The reaction was conducted at a temperature of 20 °C for 0.5 h with stirring (1200 rpm). The above reaction parameters are based on optimum conditions we have previously used for the synthesis of H₂O₂.(22, 23) The concentration of H₂O₂ was determined by titrating aliquots of the final solution after reaction with acidified Ce(SO₄)₂ (0.0085 M) in the presence of ferroin indicator. The conversion of H₂ and selectivity towards H₂O₂ were determined using a Varian 3800 GC fitted with TCD and equipped with a Porapak Q column.

H₂ conversion (Equation 1) and H₂O₂ selectivity (Equation 2) are defined as follows:

$$\text{H}_2\text{Conversion (\%)} = \frac{\text{mmol}_{\text{H}_2}(t(0)) - \text{mmol}_{\text{H}_2}(t(1))}{\text{mmol}_{\text{H}_2}(t(0))} \times 100 \text{ (eq 1)}$$

$$\text{H}_2\text{O}_2 \text{ Selectivity (\%)} = \frac{\text{H}_2\text{O}_2 \text{ detected (mmol)}}{\text{H}_2 \text{ consumed (mmol)}} \times 100 \text{ (eq 2)}$$

Degradation of H₂O₂ in a batch reactor.

Catalytic activity towards H₂O₂ degradation was determined in a similar manner to the direct synthesis activity of a catalyst. The autoclave liner was charged with H₂O₂ (50 wt. % 0.69 g), H₂O (7.82 g) and catalyst (0.01 g), with the solvent composition equivalent to a 4 wt. % H₂O₂ solution. From the solution, two 0.05 g aliquots were removed and titrated with acidified Ce(SO₄)₂ solution using ferroin as an indicator to determine an accurate concentration of H₂O₂ at the start of the reaction. The autoclave was pressurised with 2.9 MPa 5 % H₂ / CO₂ (gauge pressure). The reaction was conducted at a temperature of 20 °C, for 0.5 h with stirring (1200 rpm). After the reaction was complete the catalyst was removed from the reaction mixture and two 0.05 g aliquots were titrated against the acidified Ce(SO₄)₂ solution using ferroin as an indicator. Catalytic activity towards H₂O₂ degradation is reported herein as % degradation and accounts for hydrogenation and decomposition pathways. The reactor temperature was controlled using a HAAKE K50 bath/circulator using an appropriate coolant.

Direct Synthesis of H₂O₂ in a flow reactor.

A continuous, fixed-bed reactor was constructed for the direct synthesis of H₂O₂ using Swagelok fittings with an internal diameter of 1/4 inch. Gas flows of 5 % H₂/CO₂ and 25 % O₂/CO₂ were controlled using Brooks mass flow controllers with the pressure maintained and controlled using a back-pressure regulator at the end of the system. Pressure relief valves were included at various points throughout the system to release pressure in the case of a blockage. Water (HPLC grade) free from acid or halide additives was used as the reaction medium and pumped through the system using an Agilent 1260 series isocratic HPLC pump, a gas liquid separator (GLS) and one-way valves were placed after the MFCs to prevent any liquid from entering the MFCs during the reaction. Liquid was collected downstream before the back-pressure regulator by emptying a 150 mL GLS fitted with a valve which acted as a sample collection vessel. A schematic of the reactor is shown in Figure S.1.

A typical H₂O₂ synthesis reaction was carried out using between 0.05 and 0.25 g of catalyst, which had been pressed into a disk and sieved to a particle size of 425–600 μm. The sample was supported at the bottom of the catalyst bed in the reactor tube by glass wool. The catalyst was contained within a 10 cm stainless steel tube with an internal diameter of 1/4 inch. The reactor system was then pressurized, typically to 30 bar, with a 1:1 mixture of H₂ and O₂ from the respective CO₂ diluted cylinders. The reactor temperature was controlled using a water bath at 20 °C. When the reaction pressure and gas flows stabilised the solvent flow (typically, 0.25 - 5.0 mLmin⁻¹) was introduced into the system. Both gas and liquid flowed concurrently through the catalyst bed from top to bottom. Liquid samples were taken from the sample bomb every 10 min, and the concentration of H₂O₂ was determined by titration against an acidified dilute Ce(SO₄)₂ solution using ferroin as an indicator. During the study, the amount of H₂O₂ was quoted as the concentration formed in the reaction solution in units of parts per million (ppm). Selectivity towards H₂O₂ synthesis was determined via GC analysis, as discussed above. Evaluation of the activity of the uncharged (no catalyst) reactor towards H₂O₂ degradation and synthesis is found to be zero in both respects.

Characterisation.

Metal leaching from supported catalyst was quantified using microwave plasma atomic emission spectroscopy (MP-AES) via analysis of filtered post reaction solutions, using an Agilent 4100 MP-AES. The

concentration responses of Ni and Pd were calibrated using commercial reference standards (Agilent); in all cases $r^2 > 0.999$.

Results and Discussion.

Our initial work focused on the evaluation of 5%PdNi/TiO₂ catalysts with varied Pd: Ni ratios for the direct synthesis and subsequent degradation of H₂O₂. We used water as the solvent in the absence of halide or acid as promoters and ambient temperature both of which are not favourable conditions to suppress H₂O₂ degradation (Figure 1). (22, 23) A correlation between total Pd content and catalytic activity towards H₂O₂ synthesis was observed, with observed H₂O₂ increasing to a maximum of 312 ppm for the 0.75%Pd-4.25%Ni/TiO₂ catalyst before plateauing as the composition was varied to 1%Pd-4%Ni/TiO₂ after 30 min of reaction. Interestingly no activity towards H₂O₂ degradation, via decomposition or hydrogenation pathways, was observed for the 0.75%Pd-4.25%Ni/TiO₂ catalyst or those materials with lower Pd loadings, despite their ability to produce H₂O₂. Increasing Pd content beyond 15 % of total metal loading does not result in further rise in H₂O₂ concentration, whereas we observe the development of catalytic activity towards H₂O₂ degradation (6 %) for the 1%Pd-4%Ni/TiO₂ catalyst.

By comparison we have recently reported (23) that the well-studied 2.5%Au-2.5%Pd/TiO₂ catalyst (24, 25) prepared via a conventional wet-impregnation methodology offers significantly greater rates of H₂O₂ degradation (25 %), under identical reaction conditions indicating the beneficial effects of alloying Pd with Ni. However, despite the significantly greater activity of the supported AuPd catalyst towards H₂O₂ degradation the concentration of H₂O₂ generated (476 ppm)(23) is only slightly greater than that observed for the 0.75%Pd-4.25%Ni/TiO₂catalyst.

With the requirement for Ni to be present in order to inhibit H₂O₂ degradation pathways clear (Table S.1), we next evaluated the efficacy of the 0.5%Pd-4.5%Ni/TiO₂ catalyst over multiple sequential H₂O₂ synthesis tests under batch conditions (Figure 2). After carrying out five consecutive reactions the H₂O₂ concentration increased in a linear manner to a value of 552 ppm, with no loss in H₂O₂ selectivity (97 %) over sequential synthesis reactions. Both findings imply that there is no subsequent decomposition or hydrogenation of the H₂O₂ which is synthesised and un-stabilised in comparison to commercial samples. The high selectivity of the 0.5%Pd-4.5%Ni/TiO₂ catalyst is particularly noteworthy given the relatively unfavourable conditions utilised in this study, namely the use of ambient temperatures and a water only reaction medium.

Typically the evaluation of catalytic performance towards H₂O₂ synthesis has focussed on the use of high pressure, batch reactors.(26, 27) However, the use of such reactors inherently results in high contact times between the catalyst and synthesised H₂O₂, often leading to increased degradation via hydrogenation and decomposition pathways. Alternatively a range of membrane,(28, 29) fixed bed,(30) trickle bed(31-33) and microreactors(34, 35) have been utilised in the direct synthesis of H₂O₂. Indeed we have previously reported the efficacy of a 0.5%Au-0.5%Pd/TiO₂ catalyst, towards H₂O₂ synthesis using a fixed bed reactor, with selectivities of 80 % reached when using optimised reaction conditions.(36) However, it should be noted that when using reaction conditions similar to those used within this work (water only as solvent and ambient temperature) the 0.5%Au-0.5%Pd/TiO₂ catalyst only displayed a selectivity towards H₂O₂ of approximately 20 %, with a H₂O₂ concentration of 190 ppm produced. With the commercial production of H₂O₂ in a continuous mode likely to be favoured, due to minimisation of H₂O₂ degradation we next investigated the role of key reaction conditions on the formation of H₂O₂ over the 0.5%Pd-4.5%Ni/TiO₂catalyst in a fixed bed flow reactor. The effect of varying catalyst mass from 0.05 to 0.25 g was first investigated (Figure 3), with H₂O₂ concentration increasing in a linear manner with catalyst content up to a catalyst mass of 0.1 g, beyond which H₂O₂ concentration continues to increase but non-linearly. This in part may be related to a slight rise in activity towards the degradation of H₂O₂, as indicated by the marginal decrease in H₂O₂ selectivity at

increased catalyst mass. Which in turn results from increased contact time between reactant gases and the catalyst. Indeed, the relationship between H₂O₂ degradation activity and H₂O₂ concentration is well known.⁽¹⁵⁾ However, it is more likely, given the relatively high flow rates used within this study that the plateau observed in H₂O₂ concentration can be related to limitations associated with reactant gas diffusion to the catalyst. It should be noted that regardless of catalyst mass, selectivity towards H₂O₂ remains high, exceeding 85 %.

The effect of total reaction pressure was next investigated (Figure 4), while maintaining all other reaction conditions. As expected, an enhancement in H₂O₂ concentration was observed with increasing pressure. These results show that pressure had no effect on catalytic selectivity, which remains constant at 85 %. This is in keeping with our previous observations into supported AuPd nanoparticles, under both flow⁽³⁶⁾ and batch⁽²⁵⁾ regimes, where both H₂O₂ synthesis and degradation pathways increase proportionally with pressure.

The effect of solvent flow rate was next investigated while maintaining all other reaction conditions (Figure 5). Perhaps unsurprisingly, due to effects of dilution, we observe a decrease in H₂O₂ concentration with increasing flow rate. However, calculation of the moles of H₂O₂ produced revealed that this metric increased with solvent flow, with a maximum (0.004 mmol) observed at 3 mLmin⁻¹ solvent flow. Increasing flow rate beyond 3 mLmin⁻¹ resulted in no further increase in H₂O₂ concentration. This is ascribed to mass transfer limitations, where greater solvent flow rates and shorter residence times inhibit diffusion of reagent gases to catalytically active sites.

Finally with the requirement to re-use a catalyst successfully at the heart of green chemistry and the activity of homogeneous species towards H₂O₂ synthesis well known,⁽³⁷⁾ we next investigated catalytic activity of the 0.5%Pd-4.5%Ni/TiO₂ catalyst towards H₂O₂ synthesis for extended periods of time, under flow conditions (Figure 6). Over 10 h onstream, we observe no loss in either activity, with 80 ppm H₂O₂ produced consistently, or selectivity towards H₂O₂, indicative of the high stability of the catalyst. Furthermore, analysis of the post reaction effluent via MP-AES (Table S.2) reveals no leaching of either Pd or Ni from the catalyst surface. It should be noted that comparable concentrations of H₂O₂ to that produced over the 0.5%Pd-4.5%Ni/TiO₂ catalyst have previously been reported to offer excellent biocidal activity, with Ronen et al.⁽³⁸⁾ reporting the high efficacy of preformed H₂O₂ in the remediation of greywater.

Conclusion.

With a focus on reaction conditions considered unfavourable to H₂O₂ formation we have evaluated the efficacy of supported PdNi catalysts exposed to a successive calcination-reduction-calcination heat treatment towards the direct synthesis of H₂O₂. Catalytic activity in both a stirred autoclave reactor and using flow conditions is found to be stable, with a selectivity towards H₂O₂ exceeding 95 and 85 % in batch and flow regimes respectively. We consider that these catalysts represent a promising basis for further exploration for the direct synthesis of H₂O₂ under realistic industrial conditions.

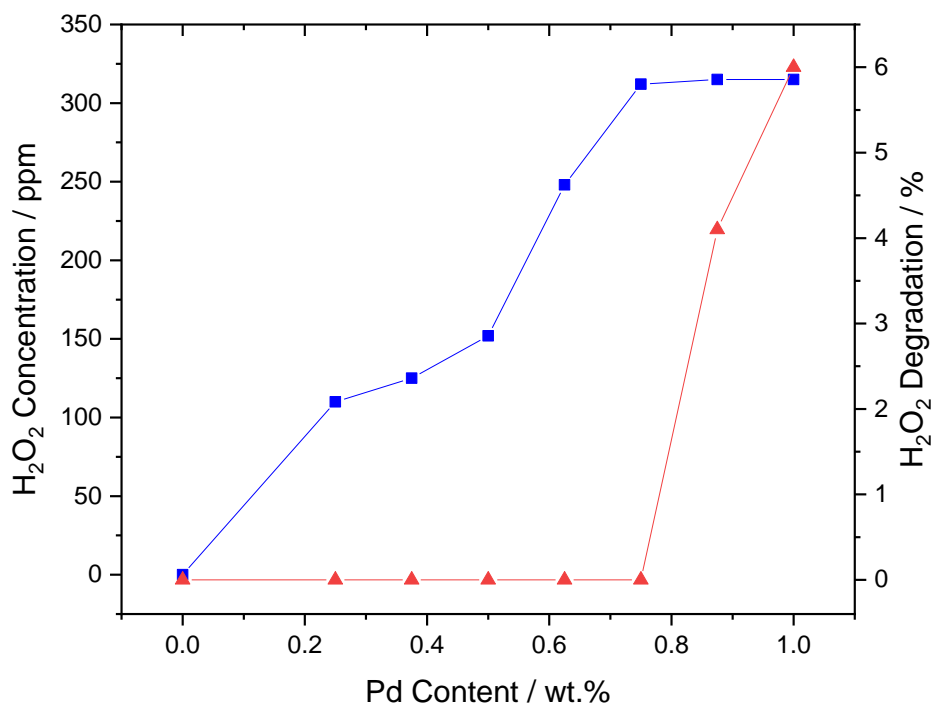


Figure 1. Catalytic activity of 5%PdNi/TiO₂ toward H₂O₂ synthesis (squares) and its subsequent degradation (triangles) as a function of Pd content, under batch conditions.

H₂O₂ direct synthesis reaction conditions: catalyst (0.01 g), H₂O (8.5 g), 5% H₂/CO₂ (420 psi), 25% O₂/CO₂ (160 psi), 0.5 h, 20 °C, 1200 rpm. H₂O₂ degradation reaction conditions: catalyst (0.01 g), H₂O₂ (50 wt. %, 0.68 g), H₂O (7.82 g), 5% H₂/CO₂ (420 psi), 0.5 h, 20 °C, 1200 rpm.

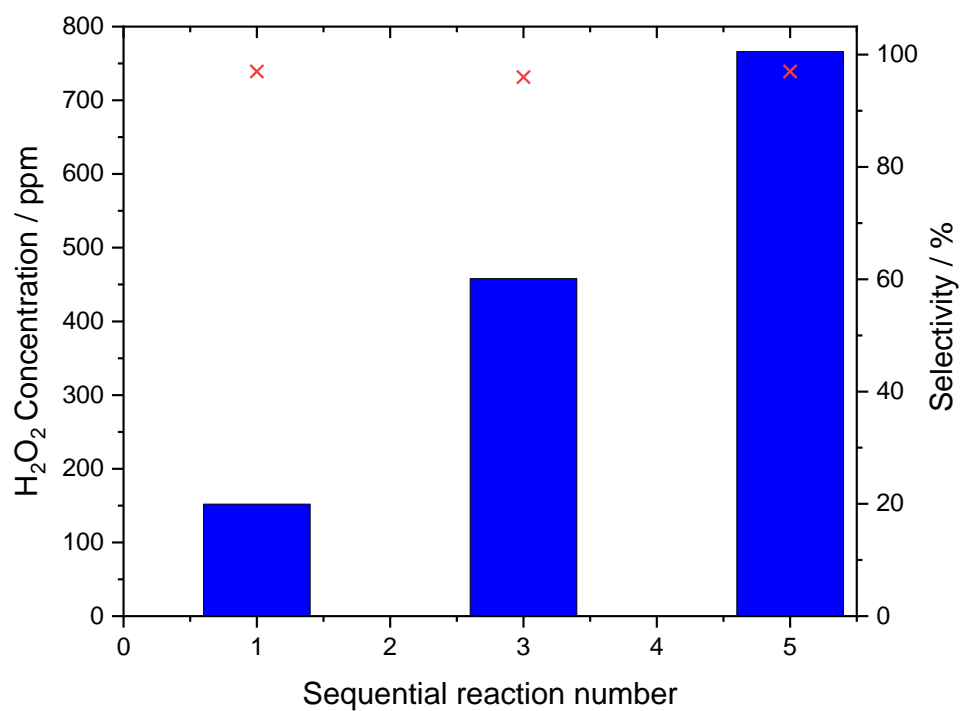


Figure 2. Sequential H₂O₂ synthesis reactions over the 0.5%Pd-4.5%Ni/TiO₂ catalyst, under batch conditions. H₂O₂ concentration (bar), selectivity towards H₂O₂ (cross).

H₂O₂ direct synthesis reaction conditions: catalyst (0.01 g), H₂O (8.5 g), 5% H₂/CO₂ (420 psi), 25% O₂/CO₂ (160 psi), 0.5 h, 20 °C, 1200 rpm.

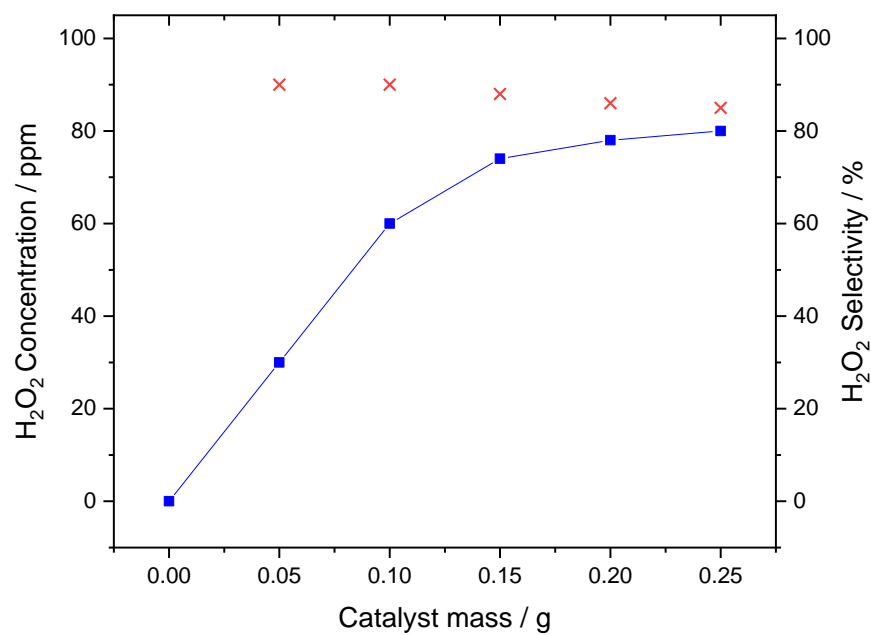


Figure 3. Effect of catalyst mass on catalytic activity towards H₂O₂ synthesis, under flow conditions. H₂O₂ concentration (squares), selectivity towards H₂O₂ (cross).
Reaction conditions: 20 °C, H₂O liquid flow rate, 1 mLmin⁻¹, 30 bar total pressure, 5% H₂/CO₂ (175 mLmin⁻¹), 25% O₂/CO₂ (35 mL min⁻¹).

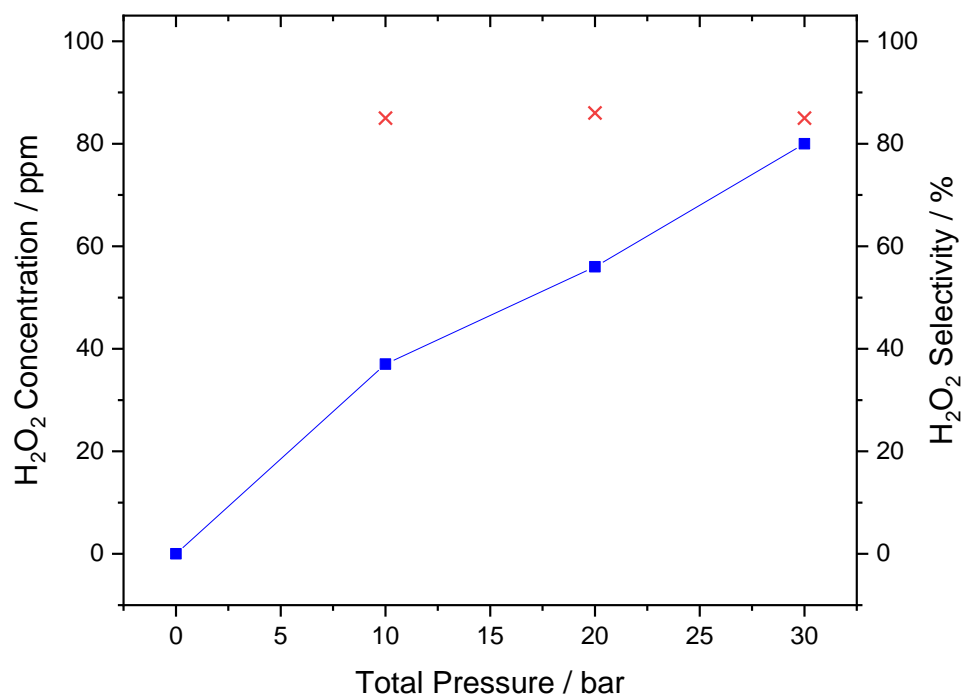


Figure 4. Effect of pressure on catalytic activity towards H₂O₂ synthesis, under flow conditions.

H₂O₂ concentration (squares), selectivity towards H₂O₂ (cross).

Reaction conditions: 20 °C, catalyst mass (0.25 g) H₂O liquid flow rate, 1 mLmin⁻¹, 5% H₂/CO₂ (175 mLmin⁻¹), 25% O₂/CO₂ (35 mLmin⁻¹).

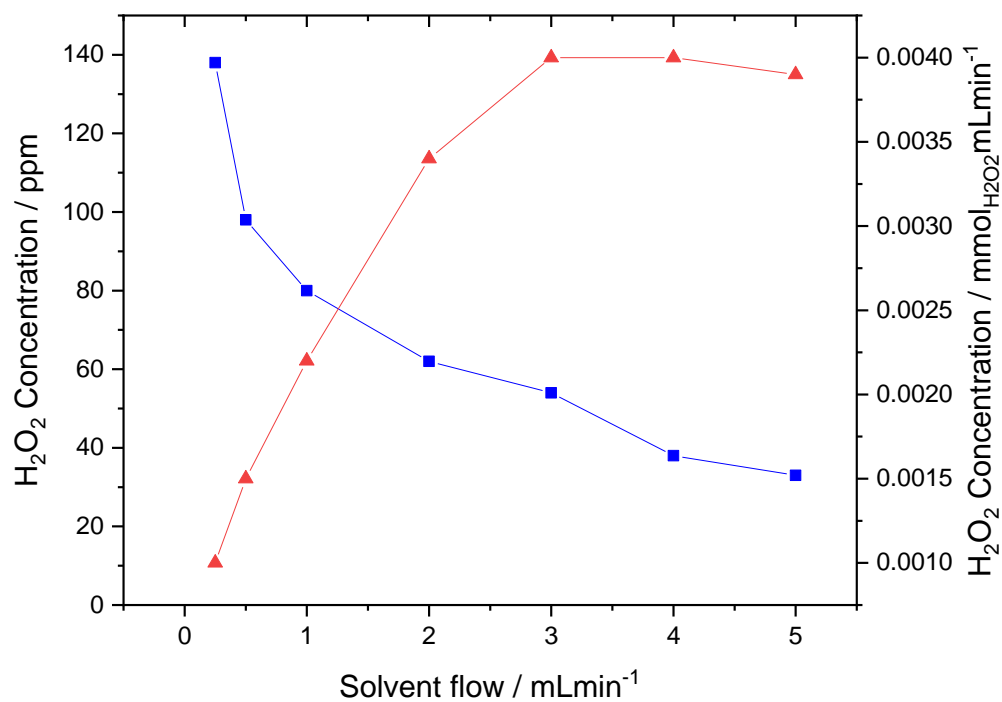


Figure 5. Effect of solvent flow rate on catalytic activity towards H₂O₂ synthesis, under flow conditions. H₂O₂ concentration as ppm (squares), H₂O₂ concentration as mmol_{H₂O₂}mLmin⁻¹ (triangles). Reaction conditions: 20 °C, catalyst mass (0.25 g) H₂O, 30 bar total pressure, 5% H₂/CO₂ (175 mLmin⁻¹), 25% O₂/CO₂ (35 mLmin⁻¹).

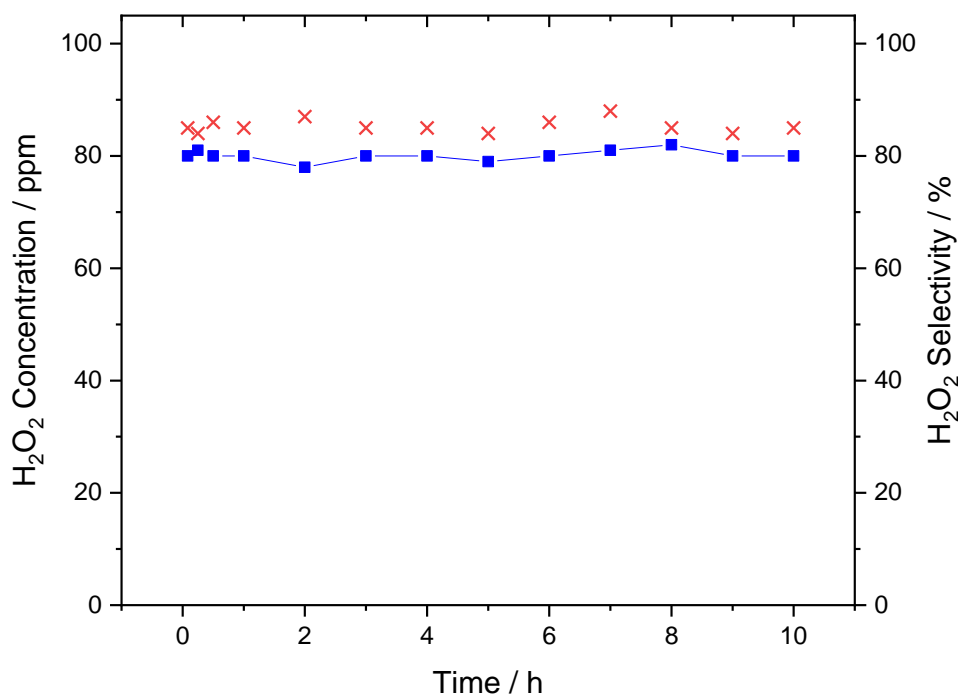


Figure 6. Catalytic activity of the 0.5%Pd-4.5%Ni/TiO₂ catalyst over 10 h onstream. H₂O₂ concentration (squares), selectivity towards H₂O₂ (cross). Reaction conditions: 20 °C, catalyst mass (0.25 g) H₂O liquid flow rate, 1 mLmin⁻¹, 30 bar total pressure, 5%H₂/CO₂ (175 mLmin⁻¹), 25% O₂/CO₂ (35 mLmin⁻¹).

Additional Information

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Data Accessibility

Readers should contact LewisR27@Cardiff.ac.uk

Competing Interests

The authors declare no competing interests.

Authors' Contributions

All authors provided substantial contributions to the conception and design, or acquisition of data, or analysis and interpretation of data, drafting the article or revising it critically for important intellectual content and final approval of the version to be published.

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