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Advances in the direct synthesis of hydrogen peroxide from hydrogen and oxygen

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ABSTRACT

The direct synthesis of hydrogen peroxide presents an attractive and atom efficient route to an important commodity chemical. The direct synthesis process has attracted considerable research interest into catalysts which could provide an alternative to the current industrial process. Many catalyst systems have been evaluated, most of which utilise Pd as the active component. The activity of the catalysts can be promoted in a number of ways, either by addition of a second metal, or by adding promoters into the reactant phase such as acid and halides. Acidic supports can increase the activity of catalysts without addition of aqueous acids by minimising the decomposition of hydrogen peroxide, and catalysts can be doped with halide ions to minimise the non-selective hydrogenation reaction. The addition of gold to form bimetallic particles has also been shown to increase hydrogen peroxide yield by increasing hydrogen selectivity without the need to add acid and halides. If the process was to ever be envisaged as a competitor to the anthraquinone process it would need to be operated in a continuous system. Recent research has focused on the use of continuous reactor systems such as membrane, fixed bed and microreactors. Recent literature regarding catalyst design and continuous process development as well as historical perspective of the process is discussed in this review.

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1. Introduction

Hydrogen peroxide, H₂O₂, is an important commodity chemical that is very familiar to the general public due to its ubiquitous use both in a domestic and industrial setting. The uses of H₂O₂ are principally in applications where its efficacy as a bleach or disinfectant is required, or which utilise its high active oxygen potential such as in the production of fine chemicals. Whilst H₂O₂ itself is considered a green oxidant (the only side product is water) the method by which H₂O₂ is manufactured, the anthraquinone process can be considered less so. Riedl and Pfleiderer of BASF developed the anthraquinone process in 1939 [1]. The process involves the hydrogenation of a substituted anthraquinone using a nickel or palladium catalyst to form the diol. The subsequent oxidation of anthraquinol in air (or oxygen-enriched air) reforms the original anthraquinone, and produces 1 molecule of H₂O₂. Whilst this process is very efficient, and produces H₂O₂ concentrations between 1 and 2 wt%, to minimise transportation cost the H₂O₂ is then worked up using

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http://dx.doi.org/10.1016/j.cattod.2014.03.011 0920-5861/© 2014 Elsevier B.V. All rights reserved. column distillations to concentrations of H_2O_2 up to 70 wt%. There are some concerns about the carbon efficiency of the process, not least the unselective hydrogenation of the anthraquinone molecule which needs to be replenished during the cycle. There are further energy concerns associated with work up and transportation as most H_2O_2 is required in concentrations between 2 and 8 wt% which means that the energy used to concentrate the H_2O_2 to transport it to point of use is essentially wasted when the H_2O_2 is subsequently diluted.

The direct synthesis of H_2O_2 from hydrogen and oxygen provides a more atom efficient route to the current commercial production process for this important commodity chemical. Currently over three million metric tonnes of H_2O_2 are produced from the indirect anthraquinone process, around 80% of which is used for fine chemical synthesis and in the paper and textile bleaching industries [2]. The increasing demand for propylene oxide means that the forecast demand for H_2O_2 is predicted to exceed 4.3 million metric tonnes in 2015 [3]. The indirect process produces concentrated H_2O_2 that has to be transported to its point of use where it is typically diluted back down to 2–8 wt%. The direct route would enable H_2O_2 production to take place at its point of use and for this reason there is significant interest in developing such a catalytic process. The potential of including H_2O_2 in large volume chemical

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synthesis has been recognised with the advent of titanium silicalite, TS-1, a zeotype material that is isostructural with ZSM-5 that is capable of effectively catalysing several different selective oxidation reactions including the epoxidation of propylene to propylene oxide (PO) and the ammoximation of cyclohexanone to its corresponding oxime [4]. In 2008, BASF and Dow Chemicals opened a joint-venture pilot plant in Antwerp, based around the direct synthesis of hydrogen peroxide and its use as an oxidant for propylene epoxidation, referred to as the Hydrogen Peroxide Propylene Oxide, HPPO process.

2. Historical perspective

The first patent detailing catalysts active for the direct synthesis reaction was granted in 1914 to Henkel and Weber [5]. The patent describes the use of Pd catalysts, and demonstrates that high concentrations of H_2O_2 can be achieved using H_2 and O_2 as the reactants. The reasons why, 100 years later, there is still no industrial process based on the direct synthesis are twofold. The first reason is one of safety, H₂/O₂ gas mixtures are explosive over a wide range of concentrations (5–95 v/v% for H_2 in O_2) and therefore H₂ and O₂ have to be diluted in "inert" gases such as CO₂ and N_2 in order to operate below the lower explosive limit [6–19]. The second reason presents a direct challenge to scientists in that catalysts used to activate molecular hydrogen (reported as the rate limiting step) [20,21] for the direct synthesis reaction are also active for the parallel combustion reaction together with the H₂O₂ hydrogenation and decomposition pathways (all thermodynamically more favoured than the synthesis reaction) to form water. A key requirement for a direct synthesis process is high H₂ selectivity (>95%) and so catalysts for this reaction must have minimal activity for H_2/O_2 combustion and have little or no activity for the non-selective hydrogenation/decomposition reactions.

2.1. Effect of acid and halides for Pd catalysts

Acid and halide promoters, present in the H_2O_2 solvent system are known to improve H_2 selectivity by suppressing the H_2O_2 hydrogenation and decomposition reactions. The studies by Pospelova in 1961 confirmed that the addition of acid (HCl, HNO₃) to supported Pd-catalysts were required to achieve high H_2O_2 yield, which is to be expected as the decomposition of H_2O_2 is base catalysed [22–24]. These findings were extended by Choudhary and co-workers, who compared the effectiveness of a series of acids on H_2O_2 decomposition activity of a 5 wt% Pd/C catalyst in aqueous reaction medium [25]. These studies revealed that acids could be classified into two groups:

Oxyacids (moderate decomposition activity decrease) – acetic acid, phosphoric acid, nitric acid, sulphuric acid and perchloric acid.

Halide acids (strongly suppressing acids with large activity decrease) – hydrochloric acid, hydrobromic acid and hydroiodic acid.

Phosphoric acid was identified as a suitable acid additive at low concentration (e.g. 0.03 M), causing negligible leaching of Pd from the catalyst into the reaction medium. The effect of halide ion addition to either the reaction medium or catalyst structure (incorporated via pre-treatment) on H_2O_2 yield has been investigated in several studies [25–30]. Studies have been carried out using a stirred glass reactor and ambient conditions for Pd supported on various metal oxides including ZrO₂, Ga₂O₃, CeO₂, SiO₂, H-Beta, ThO₂, BPO₄ and Al₂O₃. Results showed that both acid and halide additives were essential for improving H_2O_2 yield with results for halide incorporation (KF, KCl and KBr precursors) being similar in magnitude independent of whether the halide was present in the reaction medium or directly incorporated into the catalyst. The nature of the halide ions in the reaction medium was found to influence H_2 conversion where

KF > No Halide > KCl > KBr

The presence of iodide ions was detrimental to the catalyst with co-ordination to palladium resulting in surface poisoning [28]. The greatest increase in conversion was observed with the addition of KF, however the reverse effect existed for H_2O_2 selectivity where

This observation indicates that fluoride ions in fact promote the side and consecutive reaction pathways. The same sequence is reflected for H_2O_2 yield with bromide ions shown to afford a higher yield compared to chloride ions on a molar basis. This confirmed that fluoride ions in fact promoted side and consecutive reaction pathways. The same sequence is reflected for H_2O_2 yield with bromide ions shown to be more effective than chloride ions on a molar basis (0.94 mmol/dm³ KBr vs 1.5 mmol/dm³ KCl) and which is illustrate best by the decomposition pathway (previously hypothesised as being strongly dependent on H_2O_2 selectivity) [31].

Lunsford and co-workers have presented evidence of colloidal Pd being active for the synthesis of H_2O_2 [20,21,32–38]. Though use of a colloidal system on industrial scale would be extremely difficult to maintain, results from studies using different O_2/H_2 feed ratios introduced through a frit into an acidified solution (1 M HCl) are of widespread significance. Addition of either PdCl₂ or Pd/SiO₂ to HCl resulted in oxidation of Pd⁰ to form PdCl₄^{2–} ions in solution, which are subsequently reduced back to metallic Pd by H₂, leaving some metal present as colloid establishing a Pd⁰/Pd²⁺ steady state.

2.2. Hydrogen peroxide synthesis using AuPd catalysts

The first example of monometallic Au catalysts for the direct synthesis of H_2O_2 was reported by Ishihara [39] who showed that a 1 wt% Au/SiO₂ catalyst tested in the absence of halide promoters exhibited promising H_2O_2 synthesis activity (with 30% H_2 selectivity) compared to pure Pt, Pd or Ag/SiO₂ catalysts where no H_2O_2 was observed under identical reaction conditions. The rates of H_2O_2 synthesis and hydrogenation/decomposition were compared for monometallic Au catalysts with different support materials and it was concluded that basic oxides such as MgO and ZnO were unsuitable supports (forming only water) while Au/SiO₂ performed the best. The addition of 1 wt% Pd to Au/SiO₂ gave improved rates of H_2O_2 synthesis, with maximum yield reported using a Pd:Au weight ratio of 82:18.

The promotional effect on addition of Au to Pd catalysts for the direct synthesis of H_2O_2 has been extensively studied by Hutchings and co-workers over the last decade [14]. A key observation for these bimetallic catalysts has been an increase in H_2 selectivity towards H_2O_2 when compared to Pd catalysts (Fig. 1). The H_2O_2 synthesis activity of the monometallic Au and Pd catalysts were evaluated before advancing to the use of Au–Pd nanoparticles. Initial experiments were performed in a sealed stainless steel autoclave at 2°C, 37.5 bar 5%H₂/CO₂ and 25%O₂/CO₂ (1:2 molar) pressure and water (34%)/methanol (66%) solvent, resulting in improved H_2O_2 yields based on higher H_2O_2 selectivities of 61% for the AuPd/TiO₂ catalysts compared to the Pd/TiO₂ catalysts (selectivity of 21%) [7].

The nature of the alloy in the bimetallic catalysts has been studied in detail by a number of spectroscopic and microscopic techniques. X-ray photoelectron spectroscopy (XPS) indicated the development of a core-shell structure for Au–Pd particles supported on TiO₂ (Au-core Pd-shell) when the catalyst had been calcined in static air (Fig. 2). A high surface Pd/Au ratio was observed with a dramatic decrease in the intensity of the Au

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