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Direct synthesis of H_2O_2 in methanol at low pressures over Pd/C catalyst: Semi-continuous process

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ABSTRACT

The production of H_2O_2 *via* direct synthesis has been studied in depth over the last decades, due to the possibilities given by the discovery of active catalysts based on nanotechnology and selective active metals. However, the process is also complicated because of the coexistence of three phases, where mass transfer between gas and liquid (solvent) limits the concentration of O_2 and H_2 in contact with the solid catalyst sites, and subsequently the final H_2O_2 productivity. High pressures are normally used to enhance mass transfer by increasing the solubility. In this work, we explore the influence of low pressures, in order to optimise the reaction reducing mechanical requirements. Pressures from 0.1 to 0.9 MPa in a semi-continuous reactor have been tested, obtaining H_2O_2 concentrations up to 1.33 wt.% and a selectivity from 44.9% to 69.0%. A nano-Pd/C commercial catalyst and methanol as solvent have been used.

1. Introduction

Finding a green process for the production of hydrogen peroxide by direct synthesis as an alternative to the traditional anthraquinone route has fascinated scientists for decades [1]. Over 95% of the current industrial production of H_2O_2 is carried out via the anthraquinone route or Riedl–Pfleiderer process which avoids direct contact between H_2 and O_2 and offers continuous production at moderate temperatures [2,3]. Nevertheless, and this is a hackneyed argument, large amounts of by-products are produced in the traditional process, and the process requires several steps of separation and concentration, consequently requiring a rather large energy input.

Analysing the chemistry, one can easily find that the direct reaction between hydrogen and oxygen would be the simplest way to produce H_2O_2. However, the real reaction scheme is more complex due to the occurrence of simultaneous and consecutive reactions, all of them thermodynamically favoured and highly exothermic. Among these reactions are: decomposition of hydrogen peroxide, reduction of hydrogen peroxide and direct water formation by combustion.

The well-known safety issue associated with the direct synthesis process is the explosive nature of the hydrogen–oxygen mixtures. In the traditional route this problem is avoided because H_2 and O_2 are not in direct contact. Under atmospheric pressure conditions, the explosive range falls between 4.0 and 95 mol% H_2 at 25 °C [4]. Although the direct synthesis could be conducted over the Upper Flammability Limit (UFL), the operation under Low Flammability Limit (LFL) is preferred for economic (H_2 is the limitant reagent), safety (the lower the quantity of H_2, the lower is the power of an undesired explosion) and process reasons (to minimise hydrogenation of H_2O_2). This forces the use of large amounts of diluents, usually nitrogen (pure or from air), although CO_2 has also been studied [5].

An aqueous reaction medium provides the safest conditions [6–8]; however, its main drawback is the low solubility of the reacting gases, which strongly limits mass transfer and thus the rate of peroxide production. The use of alcohols [9,10] or alcohol–water mixtures [11,12] increases the solubility of the gases. As an example, Degussa/Headwaters recently announced the construction of the first pilot plant for direct synthesis of H_2O_2 to be used as an in situ source integrated into a propylene oxide plant, disclosing that methanol will be used as solvent [13,14].

The other main issue associated with the direct synthesis of hydrogen peroxide is the discovery of an active and highly selective catalyst. Most catalysts described in the literature are supported on carbon, zeolites, Al_2O_3 or SiO_2. Ntainjua et al. [15] studied the role of the support, finding that supports with low isoelectric points such as carbon and silica give the highest rates of synthesis. The active metals are usually palladium [16–18], gold [8,19] or com-

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binations of Pd + Au [10,11,20,21] or Pd + Pt [9,21]. Unfortunately, these catalysts are also responsible for the side reactions, namely the combustion of hydrogen to water and the decomposition of hydrogen peroxide. The role of size and crystalline type of the metal particles in the selectivity to H_2O_2 is still uncertain, but the effect is clear. Several authors claim the beneficial effects of nanoparticle and nanocrystals use [12,20,22]. In addition to the catalyst selection, the use of promoters and H_2O_2 protective additives is crucial, especially when using monometallic Pd catalysts. Pospelova et al. [23] early reported the beneficial effect of adding a mineral acid such as HCl in order to inhibit the decomposition of the peroxide over a Pd catalyst. More recently, the role of these so-called promoters has been analyzed in detail, and it is now generally accepted that halide anions increase the selectivity towards hydrogen peroxide, while the role of protons is to facilitate the adsorption of halide anions on the catalyst and to inhibit peroxide decomposition by decreasing its adsorption on decomposition sites [6,24,25]. The promoters are most commonly added homogenously to the solvent, although they might also be incorporated onto the catalyst via catalyst modification with similar or slightly better results [26]. On the other hand, Hutchings and his coworkers have demonstrated that it is possible to achieve high selectivities without any promoters by combining metals, such as Au–Pd catalysts [20,27].

Finally, the existence of three phases in the reactor, i.e. gases (H_2, O_2 and an inert), liquid (solvent) and solid (catalyst), usually involves important mass transfer limitations and complicates the process. Mass transfer can be enhanced by: (1) increasing mass transfer coefficient or reducing the thickness of stagnant film by stirring, (2) increasing surface area of the bubbles using low-diameter-bubble spargers or injection systems, (3) increasing the solubility of the gases by increasing the partial pressure of the gases (Henry's law); this implies the use of high pressures and subsequently the use of more expensive equipment.

In a previous work, we have demonstrated the possibility of producing H_2O_2 in both H_2 and methanol using CO_2 and N_2 as inert gases at high pressures and moderate temperatures [28]. In this work we demonstrate that H_2O_2 can be produced semi-continuously in methanol at low pressures, up to 0.9 MPa, and moderate temperatures, near ambient conditions, using a commercial Pd/C catalyst. The effect of key variables such as O_2/H_2, halide/Pd and acid/Pd ratios, reaction time and pressure has been studied. The catalyst has been characterized by TEM and SEM–EDX before and after the use in order to elucidate the effect of the support and active metal.

2. Experimental

2.1. Materials and methods

The catalyst used in this study was fine particles with an average of 5 wt.% Pd over carbon support purchased from Aldrich and used fresh for each experiment. It has been selected because it is well-known as an active catalyst, commercially available and monometallic. Research grade oxygen, hydrogen and nitrogen were purchased from BOC Gases (UK) and used without further modification. Methanol with a purity of 99.8% was used as solvent (Fischer Scientific). KI (Fluka), H_2SO_4 (Sigma) and $Na_2S_2O_3{\cdot}5H_2O$ (Fluka) were used for iodometric titration of hydrogen peroxide [11]. Water formation was determined by coulometric Karl-Fischer titration using Hydranal-Coulomat reagents (Fluka) and a Mettler-Toledo coulometer (DL37).

The bulk palladium phase in the catalyst was determined by X-ray diffraction (XRD) method using a Holland Phillips PW/1710 X-ray generator with Cu Kα radiation ($\lambda = 1.5406$ Å; 40 kV, 30 mA). The surface area and porosity of the catalysts were obtained by the BET method by measuring the adsorption of nitrogen at 77 K using a Micromeritics ASAP 2010 analyzer. TEM analysis was performed using a JEOL® JEM-1011 electron microscope (100 kV). SEM images were obtained with a FEI® Quanta 200 F ESEM microscope equipped with Everhart–Thornley and backscattered electron detectors.

2.2. Experimental set-up

Reactions were performed in a 0.1 L AISI 316 SS agitated reactor. A crosshead magnetic stirrer bar (diameter 4.5 cm) and a magnetic stirrer operating at 600 rpm were used. The gases (O_2, H_2 and N_2) were bubbled directly into the reaction medium using Brooks® mass flow controllers (Smart Mass Flow 5850). Pressure in the system was controlled by a Brooks® back pressure regulator (model 5688).

2.3. H_2O_2 synthesis

All tests were carried out at room temperature and pressures from 0.3 to 0.9 MPa. The reactor was initially passivated using 35% HNO_3 for 4 h to minimise H_2O_2 decomposition. The reaction medium was 0.03 L of methanol plus promoters (0.0125 mol H_3PO_4 and 1.2×10^{-4} mol NaBr unless otherwise stated). The catalyst (3×10^{-2} g Pd/C) was carefully added to the liquid phase before introducing the gases with a total flow of 0.125 L/min (care should be taken to avoid spontaneous combustion of methanol in contact with the catalyst). The H_2 content of the mixture was kept to 4.0% mol, the O_2/H_2 ratios varied between 2.0 and 24.0 mol/mol, and the nitrogen flow was adjusted accordingly. When the desired pressure was obtained, stirring was initiated in order to start the reaction. When the reaction was complete (reaction time 1.0 h unless otherwise stated), the products were quantified by iodometric (H_2O_2) and Karl-Fischer titration (water). Water content in the reaction medium before catalyst addition was also determined prior to each experiment.

H_2O_2 yield and selectivity are defined as follows:

$$H_2O_2\,\text{yield}\,(\%) = \frac{H_2O_2\,\text{formed}\,(\text{mol})}{H_2\,\text{added to reactor}\,(\text{mol})} \tag{1}$$

$$H_2O_2\,\text{selectivity}\,(\%) = \frac{H_2O_2\,\text{formed}\,(\text{mol})}{H_2\,\text{consumed}\,(\text{mol})} = \frac{H_2O_2\,\text{formed}\,(\text{mol})}{H_2O_2\,\text{formed}\,(\text{mol}) + H_2O\,\text{formed}\,(\text{mol})} \tag{2}$$

3. Results and discussion

3.1. Catalyst characterization

The bulk and surface properties of the fresh Pd/C catalyst are shown in Table 1. It is a highly microporous material, which provides a high specific surface area (1314 $m^2\,g^{-1}$) and a significant micropore volume (0.503 $cm^3\,g^{-1}$). SEM analysis of the catalyst showed a nanotube carbon structure (see Fig. 1). The size of the palladium particles on the fresh catalyst was found to be ca. 5 nm (see Fig. 2). The presence of the bulk metallic Pd (Pd^0) phase in the catalyst was confirmed by X-ray diffraction (XRD) as shown in Fig. 3.

A total of 15 runs have been carried out studying the effect of promoters, O_2/H_2 ratio, reaction time and pressure in yield, selectivity, conversion and peroxide concentration. A summary of these experiments is shown in Table 2.