Catalysis Today xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Direct synthesis of hydrogen peroxide using Au–Pd supported and ion-exchanged heteropolyacids precipitated with various metal ions

Simon J. Freakley*, Richard J. Lewis, David J. Morgan, Jennifer K. Edwards, Graham J. Hutchings*

Cardiff University, School of Chemistry, Main Building, Park Place, Cardiff CF10 3AT, UK

ARTICLE INFO

Article history:
Received 1 November 2013
Received in revised form 10 January 2014
Accepted 12 January 2014
Available online xxx

Keywords:
Au–Pd catalyst
Heteropolyacids
Hydrogen peroxide

ABSTRACT

The direct synthesis of hydrogen peroxide from molecular hydrogen and oxygen represents an attractive alternative to the anthraquinone process in terms of atom efficiency. Supported Au–Pd catalysts have been shown to be extremely effective in the direct synthesis process especially when supported on acidic supports. Using acidic supports aids the stabilisation of hydrogen peroxide and can also decrease the subsequent hydrogenation and decomposition reactions. We report the preparation and testing of Au–Pd catalysts prepared by ion exchange and impregnation methods with insoluble heteropolyacids as the support. The heteropolyacids contain a range of counter ions including Cs^+, Rb^+, K^+ and Ag^+. The catalysts containing Cs and Rb prepared by ion exchange were shown to be extremely active for H_2O_2 synthesis using reaction conditions that are not particularly conducive to H_2O_2 synthesis but are reaction conditions that are dictated by potential applications, such as water as a solvent and ambient temperature.

1. Introduction

Most of the H_2O_2 produced today is used in bleaching and disinfection applications such as in the textile/paper and pulp industry as there is legislative pressure to limit the use of chlorine in bleaching applications. In addition, interest in the use of H_2O_2 as a green oxidant for chemical synthesis has partly accounted for the considerable increase (4% per annum) in its global production [1]. The catalytic direct synthesis of hydrogen peroxide from molecular H_2 and O_2 represents a green and economic alternative to the current industrial anthraquinone process (sequential hydrogenation and oxidation of alkyl anthraquinone) used in the industrial production of H_2O_2 [2]. The current anthraquinone process requires large scale plants to be economically viable and also involves the production and transportation of very concentrated H_2O_2 solutions. However, most applications of H_2O_2 only require dilute hydrogen peroxide. The direct synthesis process allows for small scale production of more dilute H_2O_2 solutions at the point of use in a relatively green and inexpensive manner.

The most extensively studied catalyst for the direct synthesis reaction are supported Pd catalysts with the first patent being granted in 1914 [3]. The main challenge in the direct catalytic synthesis of H_2O_2 is the issue of hydrogen selectivity. Many catalysts, in particular Pd based catalysts, are active for the direct synthesis of H_2O_2 but are also active for the subsequent hydrogenation, decomposition and parallel combustion reactions [4–6]. These parallel and consecutive reactions all have a detrimental impact on the selectivity towards hydrogen peroxide. In order to limit the undesired side reactions which lead to a low H_2O_2 yield over Pd-only catalysts, acids and halides have to be added to the reaction mixture [7–11]. Halide incorporation into supported monometallic Pd catalysts has also been employed to suppress H_2O_2 hydrogenation/decomposition [12,13]. The addition of these additives to improve yield of hydrogen peroxide would add processing costs to an industrial process due to the additional purification required.

A major advance in hydrogen peroxide synthesis was made when it was observed that the addition of Au to Pd to form alloy nanoparticles lead to improved yield of hydrogen peroxide. Bimetallic catalysts were shown to be significantly more effective in the synthesis of hydrogen peroxide with the improved yield a result of lower hydrogen conversion compared to monometallic Pd catalysts, but with much higher selectivity towards H_2O_2 [14–16]. A systematic study of the role of the support has shown that acidic supports can help improve the yield of hydrogen peroxide by reducing the subsequent degradation of supported Au–Pd catalysts [17–19].

* Corresponding authors.
E-mail addresses: freakleys@cf.ac.uk (S.J. Freakley), Hutch@cf.ac.uk, hutch@cardiff.ac.uk (G.J. Hutchings).

http://dx.doi.org/10.1016/j.cattod.2014.01.012
0920-5861/

Park et al. [20–24] and Sun et al. [25] reported the use of monometallic Pd nanoparticles supported on insoluble heteropolyacid (HPA) catalysts for the direct synthesis of H_2O_2 in the absence of any acid and/or halide additives. Sun et al. [25] showed that Pd nanoparticles supported on HPAs comprising the Keggin structure showed higher H_2O_2 productivity and selectivity compared to other conventional monometallic catalysts supported on oxides e.g. TiO_2 and SiO_2. Park et al. studied Pd-exchanged heteropolyacids ($Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$) with varying Cs content (2.0–2.7) for H_2O_2 synthesis and found that the most acidic catalyst tested ($Pd_{0.15}Cs_{2.5}H_{0.2}PW_{12}O_{40}$) showed the best performance [24]. In a recent study we have studied the addition of Au to these systems by both impregnation and ion-exchange methods which resulted in increased hydrogen peroxide synthesis rate compared to the monometallic Pd catalysts [26]. The addition of Au also increased the activity of catalysts when compared to monometallic Pd tested at ambient temperature, with the catalysts also being substantially more active than carbon supported Au–Pd catalysts in water only solvent without the addition of any acid or halide additives which could have important potential industrial implications.

In this study we extend these studies by investigating catalysts comprising Au and Pd made by impregnation and ion exchange with heteropolyacids precipitated with a range of cations (Cs^+, Rb^+, K^+ and Ag^+) for the direct synthesis of hydrogen peroxide and we also investigate the effect of the Cs content of Au–Pd catalysts.

2. Experimental

2.1. Catalyst preparation

Au–Pd-exchanged heteropolyacid catalysts ($Pd_{0.075}Au_{0.05}X_{2.5}H_{0.2}PW_{12}O_{40}$) were prepared using an ion-exchange method previously reported [26]. A typical preparation of 1 g of catalyst is outlined as follows. $Pd(NO_3)_2{\cdot}2H_2O$ (0.005 g/3.0 ml), $HAuCl_4$ (0.249 ml, 12.25 g $HAuCl_4$/1000 ml) and either $AgNO_3$ (0.132 g), $CsNO_3$ (0.151 g), KNO_3 (0.078 g), or $RbNO_3$ (0.114 g), were dissolved separately in 5.0 ml deionised water and added drop-wise to an aqueous solution of $H_3PW_{12}O_{40}$ (0.892 g) while stirring. The resulting solution was continuously stirred while heating (60 °C, 12 h) to obtain a solid product through evaporation which was then dried (70 °C, 16 h) followed by calcination (300 °C, 2 h) to form the final catalyst. Au–Pd free heteropolyacids ($X_{2.5}H_{0.5}PW_{12}O_{40}$) were prepared in a similar manner and used as a support material for the preparation of supported Pd, Au and Au–Pd catalysts.

Supported Au–Pd catalysts comprising 2.5 wt% Au/2.5 wt% Pd/support were prepared using the following standard co-impregnation method (all quantities stated are typical for 1 g of final catalyst). $PdCl_2$ (0.042 g,) was added to aqueous $HAuCl_4.3H_2O$ solution (2.5 ml, 5 g in 250 ml) and stirred at 80 °C as previously described [26] until the Pd dissolved completely. The appropriate support, $X_{2.5}H_{0.2}PW_{12}O_{40}$ (0.95 g), was then added to the solution and stirred to form a paste. The paste was dried (110 °C, 16 h) before calcination (300 °C, 2 h) for the heteropolyacid-based catalysts.

2.2. Catalyst characterisation and testing

Hydrogen peroxide synthesis and degradation was evaluated using a Parr Instruments stainless steel autoclave with a nominal volume of 100 ml and a maximum working pressure of 14 MPa. To test each catalyst for H_2O_2 synthesis, the autoclave was charged with catalyst (0.01 g) and 8.5 g solvent (5.6 g MeOH and 2.9 g H_2O). The charged autoclave was then purged three times with 5% H_2/CO_2 (0.7 MPa) before filling with 5% H_2/CO_2 to a pressure of 2.9 MPa at 20 °C. The pressure was allowed to drop to 2.6 MPa as the gas dissolved in the solvent at 20 °C. This was followed by the addition of 25% O_2/CO_2 (1.1 MPa). The temperature was then allowed to decrease to 2 °C followed by stirring (at 1200 rpm) of the reaction mixture for 30 min. The above reaction parameters represent the optimum conditions we have previously used for the synthesis of H_2O_2 [15]. In this study, we systematically varied these reaction conditions so as to investigate the use of ambient temperature and H_2O-only solvent for the direct synthesis of H_2O_2. H_2O_2 productivity was determined by titrating aliquots of the final solution after reaction with acidified $Ce(SO_4)_2$ (0.01 M) in the presence of two drops of ferroin indicator. Catalyst productivities are reported as mol H_2O_2 kg_{cat}^{-1} h^{-1} and TOFs as mol H_2O_2 mol $metal^{-1}$ h^{-1} to 3 s.f.

H_2O_2 degradation experiments were carried out in a similar manner as H_2O_2 synthesis experiments but without adding the 1.1 MPa 25%O_2/CO_2. Furthermore, H_2O (0.68 g) from the 8.5 g of solvent was replaced by a 50 vol% H_2O_2 solution to give a reaction solvent containing 4 wt% H_2O_2. The standard reaction conditions for H_2O_2 degradation: 0.01 g catalyst, 8.5 g solvent (5.6 g MeOH, 2.22 g H_2O and 0.68 g H_2O_2 (50%)), 2.9 MPa 5%H_2/CO_2, 2 °C, 1200 rpm, 30 min. As for H_2O_2 synthesis, the standard conditions were varied in some experiments to study H_2O_2 degradation at ambient temperature and when using H_2O-only solvent.

Investigation of the bulk structure of the materials was carried out using powder X-ray diffraction (XRD) on a (θ–θ) PANalytical X'pert Pro powder diffractometer using a Cu Kα radiation source operating at 40 keV and 40 mA. Standard analysis was performed using a 40 min scan between 2θ values of 10–80° with the samples supported on an amorphous silicon wafer. Diffraction patterns of phases were identified using the ICDD data base.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed using a Bruker Tensor 27 with a HgCdTe (MCT) detector and a Harrick Praying Mantis HVC-DRP-4 cell. Sample backgrounds were determined using dried KBr.

Surface area analysis was determined using a Micromeritics Gemini 2360 analyser. A known amount of sample, 100–200 mg was placed in a straight walled tube and degassed for 1 h at 120 °C under a flow of N_2. The surface area was analysed using a single point analysis typically taking 5 points between P/P^0 = 0.05–0.1.

XPS measurements were carried out using a Kratos Axis Ultra DLD spectrometer using monochromatic AlK_α radiation (source power 120–180 W). An analyser pass energy of 160 eV was used for survey scans, and 40 eV for detailed acquisition of individual elemental regions. Samples were mounted using double-sided adhesive tape, and binding energies referenced to the C(1s) binding energy of adventitious carbon contamination taken to be 284.7 eV. Spectra were quantified using CasaXPS and surface compositions (atom %) of the different samples are presented in the table.

3. Results and discussion

3.1. Comparison of Au–Pd heteropolyacid catalysts prepared by impregnation and ion exchange for direct synthesis of H_2O_2 under standard reaction conditions

Catalysts analogous to the Cs containing heteropolyacid gold palladium materials have been prepared in this study using phosphotungstic acid precipitated with K^+, Rb^+ and Ag^+, as a catalyst support. Table 1 shows the results for the H_2O_2 synthesis and degradation activity of the bare supports used in this study. All of these supports were shown to be inactive for the synthesis of H_2O_2, but they do show some activity towards the hydrogenation/decomposition of H_2O_2. Table 1 also shows the hydrogen peroxide synthesis and degradation activity of 2.5% Au 2.5% Pd catalysts prepared by impregnation on the heteropolyacid supports prepared by precipitation. All the catalysts showed activity towards H_2O_2 synthesis and these results show that the

Please cite this article in press as: S.J. Freakley, et al., Direct synthesis of hydrogen peroxide using Au–Pd supported and ion-exchanged heteropolyacids precipitated with various metal ions, Catal. Today (2014), http://dx.doi.org/10.1016/j.cattod.2014.01.012