### **ARTICLE IN PRESS**

Catalysis Today xxx (2014) xxx-xxx



Contents lists available at ScienceDirect

### **Catalysis Today**



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

# *In-situ* synthesis of hydrogen peroxide in tandem with selective oxidation reactions: A mini-review

B. Puértolas<sup>a</sup>, A.K. Hill<sup>b</sup>, T. García<sup>a,\*</sup>, B. Solsona<sup>c,\*\*</sup>, Laura Torrente-Murciano<sup>b,\*\*\*</sup>

<sup>a</sup> Instituto de Carboquímica (ICB-CSIC), 50018 Zaragoza, Spain

<sup>b</sup> Department of Chemical Engineering, University of Bath, UK

<sup>c</sup> Department d'Enginyeria Química, Universitat de Valencia, Valencia, Spain

#### ARTICLE INFO

Article history: Received 18 December 2013 Received in revised form 25 March 2014 Accepted 27 March 2014 Available online xxx

Keywords: Green chemistry Hydrogen peroxide In-situ synthesis Selective oxidation Tandem systems

#### ABSTRACT

One-pot combination of the *in-situ* generation of hydrogen peroxide  $(H_2O_2)$  with selective oxidation reactions enhances the environmental and economic attractiveness of the use of  $H_2O_2$  as green oxidant at industrial scale. This tandem reaction improves not only the safety aspects associated to  $H_2O_2$  storage and transportation but also reduces the capital and operation costs. This review covers the progress in the field focussing on the areas of catalysis development, mechanistic understanding and engineering approaches (such as membrane reactors) for specific systems involving epoxidation of propylene oxide, hydroxylation of benzene, oxygenate synthesis from methane and Fenton processes, highlighting the main challenges to overcome in the near future.

© 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/3.0/).

#### 1. Introduction

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is currently presented as an attractive alternative to the industrial use of oxidants such as tBuOOH, N<sub>2</sub>O, NaClO, chromate or permanganate [1,2]. These stoichiometric oxidants produce large amounts of waste by-products requiring additional purification and separation steps. In contrast, hydrogen peroxide is a highly active and selective oxidation agent for many oxidation reactions with a high active oxygen content (47 wt%) producing only water as a co-product [3]. Additionally, hydrogen peroxide normally presents a higher oxidation potential than molecular oxygen, being efficient in a wide range of reaction conditions both acidic and basic. An important breakthrough in this field took place in 2008 with the commercialisation of the epoxidation of propylene with  $H_2O_2$  to obtain propylene oxide (HPPO process) using titanium silicalite (TS-1) as a catalyst. Currently there are two HPPO-process plants jointly developed by BASF and Dow in Belgium and Thailand which finished their start-up in 2008 and 2011, respectively [4,5].

http://dx.doi.org/10.1016/j.cattod.2014.03.054

Currently, hydrogen peroxide is industrially produced via the anthraquinone route. Simplistically, in this process, an alkyl anthraquinone is used as a carrier which is firstly hydrogenated and later oxidised, releasing hydrogen peroxide [3]. One of the main advantages of this system is its capability of producing highly concentrated H<sub>2</sub>O<sub>2</sub> which is normally marketed with concentrations ranging from 35 to 50 wt% or even above, however, the transportation and storage of H<sub>2</sub>O<sub>2</sub> in concentrated form presents associated safety and economic issues. Currently, there is great scientific and industrial interest in the direct synthesis of hydrogen peroxide from molecular hydrogen and oxygen as a way of resolving its current challenges and potentially reducing its price [6,7]. Additionally, despite the relatively low concentration of H<sub>2</sub>O<sub>2</sub> achieved during its direct synthesis compared to the high concentration solutions via the anthraquinone route, it aligns with the requirement for oxidation reactions (3-5 wt%).

Most of the current research in the area of direct synthesis of  $H_2O_2$  as an oxidising agent focuses on the development of highly active and selective noble metal catalysts, with emphasis on gold and gold-palladium due their high yield stability [6,8,9]. Despite recent progress in the area [7], its large-scale application is mainly limited by its parallel decomposition into  $H_2$  and water on the metal surface, decreasing the hydrogen efficiency of the process compromising its economic feasibility. Different strategies are currently being explored to overcome this problem [6], being the one-pot direct synthesis and utilisation of  $H_2O_2$  one of the most elegant

0920-5861/© 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/3.0/).

Please cite this article in press as: B. Puértolas, et al., *In-situ* synthesis of hydrogen peroxide in tandem with selective oxidation reactions: A mini-review, Catal. Today (2014), http://dx.doi.org/10.1016/j.cattod.2014.03.054

<sup>\*</sup> Corresponding author. Tel.: +34 976 733977.

<sup>\*\*</sup> Corresponding author. Tel.: +34 96 35 43735.

<sup>\* \* \*</sup>Corresponding author. Tel: +44 125 385857.

*E-mail addresses*: tomas@icb.csic.es (T. García), benjamin.solsona@uv.es (B. Solsona), ltm20@bath.ac.uk (L. Torrente-Murciano).

2

### **ARTICLE IN PRESS**

B. Puértolas et al. / Catalysis Today xxx (2014) xxx-xxx

approaches [10–12]. In this way, *in-situ* generated hydrogen peroxide from molecular oxygen and hydrogen is simultaneously used for oxidation without the requirement of intermediate purification and/or separation steps. This integration of processes presents obvious advantages towards the reduction of the capital and operational costs which are expected to further the enhancement of the economic attractiveness of the use of hydrogen peroxide at industrial scale. Further safety benefits are gained by the lack of transportation and storage of hydrogen peroxide. Additionally, a controlled feeding of the desired concentrations of hydrogen peroxide in the system can be naturally achieved and tuned depending on the oxidation requirements. Considering these advantages, it is not surprising that the study of oxidation reactions using in-situ generated hydrogen peroxide has always been of great scientific interest, especially within the green chemistry movement. Consequently, the number of articles devoted to this tandem reaction has exponentially increased since the first studies in the 90s with most of the early progress covered in a review article by Clerici et al. in the late 90s [10]. Since then, significant progress has taken place in the areas of catalyst development, mechanistic understanding and engineering approaches such as the application of membrane reactors which are reviewed here. Focus has been directed towards specific systems involving epoxidation of propylene oxide, the hydroxylation of benzene, oxygenate synthesis from methane and Fenton processes due to their industrial potential. This review also highlights some of the current limitations in this tandem system that must be considered for future developments such the lower overall yields to oxidation products compared to the use of pre-synthesised hydrogen peroxide, the high flammability of  $H_2/O_2$  mixtures and  $H_2$ efficiency.

#### 2. Propylene epoxidation to propylene oxide

The selective oxidation of hydrocarbons is one of the most important processes for producing oxygenates, which are used as key intermediates in organic synthesis. One example of a high value oxygenate is propylene oxide (hereafter denoted as PO) which is mainly used as a feedstock for producing urethane polyols and propylene glycol.

The selective oxidation of propylene with molecular oxygen has been demonstrated to be very difficult to carry out as low yields and selectivity to PO are obtained. Thus, most of the industrial processes for PO production use clorohydrin or hydroperoxides in a two-stage process, which involves additional separation and/or purification units that increase the overall cost of the process. Recently a new process called hydrogen peroxide to propylene oxide (HPPO process) based on the selective oxidation of propylene with hydrogen peroxide has been implemented in Belgium and Thailand [4,5]. The HPPO process presents significant advantages from an economical and environmental point of view over former systems based on clorohydrin or tert-butyl peroxide such as the lower purification costs, the decrease in wastewater and the required energy input.

An interesting alternative to the HPPO process is the synthesis of PO by selective oxidation with *in-situ* generated  $H_2O_2$  from oxygen and hydrogen, which can be undertaken in both liquid or vapour phase. Most of the studies in this area involve the use of metal nanoparticles supported on titanium-based materials as catalytic systems. Gold attracts most of the attention, however, there are also studies based on silver or other precious metals such as platinum or palladium. It is generally agreed that the role of the metallic species is mainly to produce hydrogen peroxide from  $H_2$  and  $O_2$  which is then converted into hydroperoxide-like species at the Ti sites of the support [8,13–28]. However, the metallic species can also be involved in the epoxidation reaction itself. An IR spectroscopic study [29] showed that the presence of gold nanoparticles

on titania also catalyses the reaction between propylene and titania sites forming a bidentate propoxy species, similar to that formed by prolylene adsorbed on titania. The gold nanoparticles also catalysed the consecutive oxidation of the bidentate species to form carbonate/carboxylate species, which could be the cause of catalyst deactivation as discussed below. In the presence of H<sub>2</sub> and O<sub>2</sub>, the intermediate bidentate propoxy species can desorb from the catalyst surface forming peroxide species over gold as the rate determining step [22,29,30]. Therefore, the mechanism of epoxidation of propylene over metallic-based catalysts can be simplistically described by the following steps [31,32]: (i) Propylene adsorbs on the titania-based support to produce bidentate propoxy species. (ii) Simultaneously, hydrogen and oxygen produce hydroperoxide-like species (OOH or H<sub>2</sub>O<sub>2</sub>) on the metallic surface and (iii) The peroxide species aid the desorption of the bidentate propoxy species from the catalyst, producing propylene oxide and water and restoring the support to its original state. Alternatively, these bidentate propoxy species could be further oxidised to produce strongly adsorbed carboxylate species causing the loss of the activity of the catalyst. Despite the synergetic role of the support and the metal nanoparticles in the tandem reaction, the effect of both is going to be considered separately for the sake of structure and clarity, however, one should consider both simultaneously when designing selective and active catalytic systems.

#### 2.1. The effect of the support

The catalytic support has two main roles in the tandem in-situ generated  $H_2O_2$  and epoxidation of propylene. It contains the titanium active sites for the adsorption of propylene and its further epoxidation and it is responsible of the dispersion of the metal species. Additionally, depending on its structure, the support can also play a role in the catalyst deactivation. The presence of Ti sites in tetrahedral-coordination is crucial for catalytic activity in detriment to those Ti sites in octahedral coordination. Tetrahedral coordinated Ti sites are found not only to be favourable for attaining small gold nanoparticles and consequently a high metal dispersion [33] but also to be involved in the adsorption of propylene [14,31,34]. Early studies on the effect of the support showed that isolated and/or highly dispersed tetrahedral titanium sites can be obtained in either mesoporous titanosilicate (TiO<sub>2</sub>-SiO<sub>2</sub>) or microporous titanosilicate (TS-1). Well dispersed titanium-containing supports result in catalysts more resistant to deactivation and able to obtain slightly higher PO yields in spite of the low propylene conversion values achieved (Table 1) [35]. However, these tetrahedral sites together with neighbouring surface hydroxyl groups (Ti-OH, Si-OH) are found to be responsible of the readsorption of PO [36], which further causes catalyst deactivation by producing bidentate propoxy species, carbonates, carboxylates, and oligomers on the catalyst surface [13-17,30,35-38]. Accordingly, it was observed that deactivation with time on stream occurs even when nonporous silica was used as a major carrier of Au catalysts [39,40], indicating that both the surface properties and the hydrophobic character rather than steric structure of the Ti-containing supports are related to the deactivation. Further confirmation of the effect of silanol sites (Si-OH) in the catalyst deactivation [17,38,39,41-43] was given by Qi et al. [44] who observed by IR and HRTEM analyses that the interaction between titanium oxides and commercial non-porous silica can be intensified to form more isolated TiO<sub>4</sub> units with tetrahedral coordination with an increase in heat treatment temperature, diminishing catalyst deactivation. Likewise, the deactivation of Au/TiO<sub>2</sub>-SiO<sub>2</sub> catalysts can be controlled by adding trimethylamine in the reaction feed [41,45], since in this way, silanol sites could be masked. Similarly, Nijhuis et al. [46] observed that the presence of water in the feed gas stream can also suppress the catalyst deactivation

Please cite this article in press as: B. Puértolas, et al., *In-situ* synthesis of hydrogen peroxide in tandem with selective oxidation reactions: A mini-review, Catal. Today (2014), http://dx.doi.org/10.1016/j.cattod.2014.03.054

Download English Version:

## https://daneshyari.com/en/article/6505196

Download Persian Version:

https://daneshyari.com/article/6505196

Daneshyari.com