



# Role of size and pretreatment of Pd particles on their behaviour in the direct synthesis of H<sub>2</sub>O<sub>2</sub>

Salvatore Abate\*, Katia Barbera, Gabriele Centi, Gianfranco Giorgianni, Siglinda Perathoner

University of Messina, ERIC aisbl and, INSTM/CASPE, Section Industrial Chemistry, V.le F. Stagno D'Alcontres 31, 98166 Messina, Italy

## ARTICLE INFO

### Article history:

Received 30 November 2015

Revised 21 December 2015

Accepted 26 December 2015

Available online 13 January 2016

### Keywords:

H<sub>2</sub>O<sub>2</sub> direct synthesis

Pd nanoparticles

Kinetics of H<sub>2</sub>O<sub>2</sub> synthesis

Pd role in H<sub>2</sub>O<sub>2</sub> synthesis

## ABSTRACT

Two families of catalysts, based on Pd nanoparticles supported on ceramic asymmetric tubular alumina membranes, are studied in the direct synthesis of H<sub>2</sub>O<sub>2</sub>. They are prepared by depositing Pd in two ways: (i) reduction with N<sub>2</sub>H<sub>4</sub> in an ultrasonic bath and (ii) by impregnation-deposition. The first preparation leads to larger particles, with average size of around 11 nm, while the second preparation leads to smaller particles, with average size around 4 nm. The catalytic membranes were tested as prepared, after thermal treatment in air and after further pre-reduction with H<sub>2</sub> in mild (100 °C) conditions. Samples were characterized by TEM, CO-chemisorption monitored by DRIFTS method and TPR, while catalytic tests have been performed in a semi-batch recirculation membrane reactor. Experimental catalytic results were analysed using two kinetics models to derive the reaction constants for the parallel and consecutive reactions of the kinetic network. Smaller particles of Pd show lower selectivity due to the higher rate of parallel combustion, even if the better dispersion of Pd and thus higher metal surface area in the sample lead to a productivity in H<sub>2</sub>O<sub>2</sub> similar or even higher than the sample with the larger Pd particles. Independently on the presence of smaller or larger Pd nanoparticles, an oxidation treatment leads to a significant enhancement in the productivity, although the catalyst progressively reduces during the catalytic process. The inhibition of the parallel combustion reaction (to water) induced from the calcination treatment remains after the in-situ reduction of the oxidized Pd species formed during the pre-treatment. This is likely due to the elimination of defect sites which dissociatively activate oxygen, and tentatively attributed to Pd sites able to give three- and four-fold coordination of CO.

© 2016 Science Press and Dalian Institute of Chemical Physics. All rights reserved.

## 1. Introduction

H<sub>2</sub>O<sub>2</sub> is a key reactant for the development of new sustainable chemical processes [1–6] and for a new energy-chemistry nexus [7,8], because it allows to develop cleaner and resource/energy efficient chemical productions of large-volume chemicals (propylene oxide, caprolactam, phenol) as well as cleaner processes for the environmental protection (water and soil treatment). The direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> will allow to progress further in this direction, because it reduces the energy intensity, process complexity and environmental impact with respect to the current process of H<sub>2</sub>O<sub>2</sub> synthesis based on methyl anthraquinone, in addition to potentially decrease the process cost.

Several recent reviews have analysed the mechanistic, catalytic and reaction engineering aspects of this process [5,9–14]. However, still no commercial process exists, notwithstanding the advances in these areas, for various reasons, one of which being the

necessity to intensify process productivity strongly limited from the large explosivity region of H<sub>2</sub>/O<sub>2</sub> mixtures. One of the directions to overcome this limit is to develop a process based on membranes, which separate physically the H<sub>2</sub> and O<sub>2</sub> flows. We have studied in the past several aspects of the catalytic chemistry of membranes for the direct synthesis of H<sub>2</sub>O<sub>2</sub>, either in the form of a supported thin film of Pd or of nano particles of Pd supported on a ceramic membrane [15–19]. The first type of membrane is preferable in terms of safety, but are strongly limited from the rate of hydrogen transport through the membrane at the low temperatures (around room temperature) used for the direct H<sub>2</sub>O<sub>2</sub> synthesis.

Another general issue in this process of direct H<sub>2</sub>O<sub>2</sub> synthesis is that the parallel and consecutive reactions of water formation from H<sub>2</sub>/O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>, respectively, are also catalysed from the Pd nanoparticles active in H<sub>2</sub>O<sub>2</sub> synthesis, even though the specific nature of these nanoparticles (oxidation state, presence of an alloy with Au or Pt, size and crystalline faces exposed, interaction with the support) influences their rates of reaction and in turn the selectivity, productivity and stability as well. There is thus a great role of the catalyst nanostructure in determining the catalytic performances, even if the exact correlation of these aspects with the

\* Corresponding author. Tel: +39 090 6765609; Fax: +39 090 391518.

E-mail address: [abates@unime.it](mailto:abates@unime.it) (S. Abate).

catalytic performances is still under discussion. For example, it is still unclear whether an optimal size of Pd nanoparticles exists.

Several studies, as discussed in the cited reviews [5,9–14], have analysed some aspects of this complex catalytic chemistry. We may note, however, that the catalyst changes during reaction, and as a function of the reaction conditions, while these aspects have been typically limited considered [20–23]. There is likely an influence of the reaction medium and reaction conditions on the redox dynamics of the Pd nanoparticles [21,24], but more specific indications are not present in literature.

The initial state of the Pd nanoparticles depends likely on the redox pretreatment of the Pd nanoparticles [22]. The analysis of the change in the dynamics of catalyst performances during the initial stage of reaction as a function of the pretreatment of the Pd nanoparticles could provide thus indications both on the influence of the reaction medium and conditions on the active state of the catalyst and on the relationships between catalyst properties and catalytic behaviour.

The aim of this work is thus to analyse these aspects, with reference, in particular, to Pd-only nanoparticles over ceramic membranes, for the motivations commented above. The effect of the pretreatment of Pd nanoparticles on the dynamics of change of catalytic performance during the direct synthesis of  $H_2O_2$  is studied and modelled from the kinetics point of view, because this type of analysis provides further quantitative support to the relationship between catalyst properties and catalytic performances.

While other studies on the kinetics of  $H_2O_2$  direct synthesis are present in literature [16,25–27], this specific aspect of kinetic modelling of the reaction to account the change of the catalyst properties during reaction, and as a function of catalyst pre-treatment, was not previously analysed. In addition, it is relevant to study this aspect on the catalytic membranes discussed above (motivated by safety reasons), because the dynamics of change depend strongly on the type of support [28]. We compared here samples having similar Pd loading, but different preparations. The loading of Pd was chosen to have a good activity, but at the same time relatively good dispersion of Pd nanoparticles.

## 2. Experimental

### 2.1. Preparation of the catalysts

Asymmetric porous  $\alpha$ - $Al_2O_3$  tubes provided by INOPOR, Germany, were used as the substrate for the deposition of Pd dispersed particles. The alumina tube is characterized by a macroporous support (3  $\mu$ m pore size, about 1.5 mm thickness) with a final  $\alpha$ - $Al_2O_3$  mesoporous layer (pore size 70 nm, about 20-micron thickness) on the internal side of the tube. The inner and outer diameters of the tubes were 0.7 and 1.0 cm respectively, and the length of the tube was 13 cm.

The Pd is deposited in this thin mesoporous alumina layer, as shown by Pd EDX mapping. This could be easily accounted by considering the strong capillary forces present during deposition of Pd. On the other hand, only this layer is wetted during the catalytic tests, and thus Pd which is not deposited in this layer would be inactive. We have used tubular membranes with the final membrane layer both on the external or internal side of the alumina tube. Although the former is preferable (higher geometrical area), the membranes with the inner final alumina layer have much less cracks and holes with respect to those with the final layer on the external side of the tube. For this reason, we have deposited Pd on tubular membrane support having the final mesoporous layer in the inner side.

The ceramic tubes, before Pd deposition, were washed with isopropanol in a sonic bath for 10 min and dried for 1 h at 110 °C. The active phase was deposited on the inner side of the tube. Two dif-

ferent preparation techniques were compared: (1) reduction with  $N_2H_4$  in an ultrasonic bath (NR); (2) impregnation-decomposition (ID).

The preparation starts with a verification of the quality of the membrane alumina tubes by the bubble point method, which was used to locate possible macro-defects on the  $Al_2O_3$  tubular support. The method is based on the immersion of the tube in an ethanol/water mixture. The tube is pressurized (with  $N_2$  up to a pressure of 5 bar, about 2 times higher than the pressure used for  $H_2O_2$  direct synthesis) and the uniformity of bubble formation is monitored to evidence cracks and holes in the ceramic membrane. This is the most common method used to identify macro defects present in the final layers of tubular-type membranes.

#### 2.1.1. Reduction with $N_2H_4$ in an ultrasonic bath (NR)

Two solutions were prepared. Solution A is an HCl aqueous solution (0.1 N) containing 2 wt%  $PdCl_2$ , while solution B is an aqueous 2 M solution of hydrazine. The alumina tube, whose external side was protected with Parafilm, was immersed in solution A for 3 min. After washing with distilled water, the tube was then immersed in solution B for 3 min and further washed with distilled water. Both containers with the two solutions are immersed in a sonic bath used to create the appropriate mixing. This cycle was repeated five times, in order to increase the amount of Pd deposited up to 3.5 mg. The sample was finally washed with distilled water and dried at 110 °C for 1 h. Pd loading was estimated by weighting. The catalytic membrane is named **NR**. This membrane was tested in  $H_2O_2$  direct synthesis and then was calcined at 450 °C (1 °C/min) for 6 h. The latter sample is indicated as **NRC**.

#### 2.1.2. Impregnation-decomposition (ID)

A Pd(II)-acetate precursor was dissolved in acetone and poured in a graduate cylinder together with the ceramic tube. The solution wets the membrane, from the macroporous side, penetrating into the pores and is concentrated into the layer with the finest pores, inside of the tube. The solvent acetone is constantly evaporated from the inner side by a  $N_2$  stream (2.5 L/min). About 8.5 mL of precursor solution is used to achieve a Pd loading of 4 mg, confirmed by weighting the final samples. The ceramic tube was dried at 50 °C in a natural convection oven overnight. After completing the drying, the membrane was placed into a tubular oven and heated up to 250 °C for 3 h in  $N_2$  flow for decomposition of the Pd precursor. The catalytic membrane is named **ID**. The catalyst was tested in  $H_2O_2$  direct synthesis and then the same heating treatments described above for sample NRC were used. The catalytic membrane is indicated as **IDC**. This membrane was also tested after reduction in  $H_2$  at 100 °C of the IDC sample, i.e., calcined at 450 °C and then reduced at 100 °C in  $H_2$ . This sample is indicated **IDCR**. Table 1 provides a summary of the different catalytic membranes utilized.

### 2.2. Testing

Catalytic tests were carried out at room temperature in a semi-batch recirculation membrane reactor, as earlier described [16].  $H_2$  was fed from the external side of the membrane at 2 bar, after purging the line. Oxygen was bubbled in a 100 ml anhydrous methanol solution containing 100  $\mu$ L of  $H_2SO_4$  96 wt% and 6 mg KBr as promoters. The solution was continuously circulated in the inner side of the ceramic tube by a peristaltic pump (44 mL/min) equipped with special Tygon1 MH tubing. The estimated  $O_2/H_2$  ratio used during the catalytic tests, based on the gas solubilities and reactor model, is about 0.88 in the inner side of membrane.  $H_2O_2$  concentration was monitored by iodometric titration, using an automatic titration apparatus (Metrohm, 794 Basic Titrimo). Water concentration was determined by a KF coulometer (Metrohm).

# دانلود مقاله



<http://daneshyari.com/article/63725>



- ✓ امکان دانلود نسخه تمام متن مقالات انگلیسی
- ✓ امکان دانلود نسخه ترجمه شده مقالات
- ✓ پذیرش سفارش ترجمه تخصصی
- ✓ امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
- ✓ امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
- ✓ دانلود فوری مقاله پس از پرداخت آنلاین
- ✓ پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات