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Direct synthesis of H_2O_2 on monometallic and bimetallic catalytic membranes using methanol as reaction medium

Stefano Melada [a], Francesco Pinna [a], Giorgio Strukul [a,*], Siglinda Perathoner [b], Gabriele Centi [b]

[a] *Department of Chemistry, University Ca' Foscari, INSTM Consortium R.U. of Venice, Dorsoduro 2137, 30123 Venezia, Italy*
[b] *Department of Industrial Chemistry and Materials Engineering, University of Messina, INSTM Consortium R.U. of Messina, Salita Sperone 31, 98166 Messina, Italy*

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Abstract

Tubular catalytic membranes (TMCs) active in the direct synthesis of hydrogen peroxide were prepared, characterized, and tested using methanol as the reaction medium. Low hydrogen peroxide selectivity was found when only palladium was used as a catalyst, whereas palladium/platinum bimetallic samples gave higher productivity and selectivity, with an optimum molar ratio of 18. The H_2O_2 decomposition rate is influenced by the feed gases. O_2 improves H_2O_2 stability, whereas H_2 causes hydrogen peroxide to decompose at a higher rate. The most likely decomposition pathway should be the reduction of H_2O_2 to water by H_2. Bromide ion was used as a promoter and when used in excess (60 ppm) causes a decrease in overall catalytic activity.

Keywords: Hydrogen peroxide; Direct synthesis; Membranes; Palladium; Bimetallic catalysts

1. Introduction

The direct synthesis of hydrogen peroxide from hydrogen and oxygen has been known since the beginning of the 20th century [1] and is in principle a more economic and environmentally acceptable alternative to the classic antraquinone route. However, to date it has found no industrial applications, despite a large number of patents filed over the past 30 years [2–15]. This is due to two main reasons: (i) the need to avoid formation of explosive H_2/O_2 mixtures and (ii) the still unacceptably low selectivity of the reaction (whose main product is water). Nonetheless, the interest in the direct synthesis remains very high, as witnessed by Degussa's recent announcement of the constitution of a joint venture with a nanocatalysis firm to develop and commercialize a direct synthesis process [16].

Scientific works in the open literature began appearing only recently [17–23], although Pospelova was a pioneer in the field during the 1960s [24–26]. Recently, the use of specially designed membranes [27,28] has attracted considerable interest because it provides a promising approach to overcoming, at least in principle, the problems of safety and selectivity [10, 11,27].

Recently [28–30] we reported the use of carbon-coated ceramic membranes containing palladium, which allow the direct synthesis of hydrogen peroxide. These membranes were designed to feed hydrogen from inside the membrane toward the external part, where an oxygen-saturated aqueous solution comes in contact with the Pd active phase. This concept addresses the safety issue, while maintaining interesting productivity, especially if the reaction is carried out under pressure. However, an evaluation of the selectivity of this catalyst design remains crucial. In this paper we address this point and report the use of these catalytic membranes in methanol. This allows reliable measurement of H_2O_2 selectivity with the additional advantage of obtaining H_2O_2 solutions in an organic solvent. In principle, this could lead to an easier concentration step (MeOH instead of H_2O), a factor that can strongly affect the price of hydrogen peroxide given the current production technology.

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[*] Corresponding author.
E-mail address: strukul@unive.it (G. Strukul).

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2. Experimental

The membranes were 10-cm-long asymmetric α-Al_2O_3 tubular supports externally coated with a synthetic carbon layer. The carbon loading was in the range of 70–80 mg for each tube. The coating was performed by MAST Carbon Ltd., Guildford, UK, and the alumina support was supplied by Hermsdörfer Institut für Technische Keramik-HITK, Hermsdorf, Germany.

2.1. Sample preparation

The metal deposition procedure was as described previously [29]. Carbon-coated membranes (CAMs) were activated in CO_2 at 850 °C and then impregnated by a deposition–precipitation method (a classical method for obtaining eggshell-type catalysts) [31–33]. This technique consists of two steps: (i) basification of the membrane surface by soaking in a NaOH solution (0.1 M) and (ii) deposition of $Pd(OH)_2$ by precipitation from an acidic $PdCl_4{}^{2-}$ solution (40 ppm Pd). The pH of the starting Pd(II) solution was 0.7. Bimetallic samples were prepared similarly. In this case the metal salt solution was a $PdCl_4{}^{2-} + PtCl_6{}^{2-}$ solution with the appropriate Pd/Pt molar ratio.

During impregnation, $Pd(OH)_2$ (with or without $Pt(OH)_4$) was deposited into the pore network of the external membrane layer. After metal(s) deposition, membranes were dried, reduced at room temperature in H_2 flow, and eventually washed with distilled water to remove chloride ions. Pd loading was around 2.5 wt% with respect to carbon loading. The Pd/Pt ratio was either 10 or 18. Hereafter, the different samples are denoted as tubular membrane catalysts (TCMs).

2.2. Characterization

Scanning electron microscopy (SEM) images were obtained with a Jeol JSM 5600 LV (low-vacuum) microscope. The membrane was gently broken into several chips (10–20 mm) that were subsequently attached on a support with conductive glue and put in the microscope chamber.

Transmission electron microscopy (TEM) images were obtained with a Jeol 3010, operating at 300 kV, equipped with a Gatan slow-scan CCD camera (model 794) and an Oxford Instrument EDS microanalysis detector (model 6636). Each membrane surface was scratched, and the resulting powder was dispersed in isopropyl alcohol, ultrasonicated for 5–10 min so that particles would not settle down, and then deposited onto a holey carbon film.

CO chemisorption measurements were carried out at 25 °C with a pulse technique on a homemade apparatus equipped with a thermostatted reactor and a ESS Genesys quadrupole mass spectrometer interfaced to a computer for data collection and analysis. CO^+ fragment ($m/z = 28$) was used for quantitative measurements. A 2/1 chemisorption stoichiometry was assumed for both CO/Pd [34] and CO/Pt [35].

Calibrations were carried out after each measurement by injecting a known amount of CO from a calibrated loop. A specially shaped sample holder was used to analyze the TCM as a whole. Because CO is strongly chemisorbed on Pd and Pt, all samples were characterized after the catalytic tests. Before each measurement, samples were reduced in situ by passing a 5% H_2/He mixture at 25 °C, and then thoroughly evacuated with He.

Metal loading was determined by atomic absorption spectroscopy from the solutions used for metal deposition on the membranes. Differences between metal concentration before and after impregnation gave the amount of loaded metal. The efficiency of this method has been proven previously [30].

2.3. Catalytic tests

Tests were carried out in a semibatch recirculation reactor as described previously [29], in which the membrane was sealed in a tubular holder. From the inner side, H_2 was fed at constant pressure (3 bar) while an oxygen-saturated acidic solution was continuously circulated on the outer side of the membrane (on which Pd was deposited) by a peristaltic pump (25 ml/min) equipped with special Tygon® MH tubing. The circulating solution was 100 ml of anhydrous methanol containing 6 ppm Br^- and 2.8 g/l H_2SO_4. Before the catalytic experiments were begun, the catalyst surface was activated by circulating an oxygen-saturated solution on the membrane already placed in the reactor and pressurized with N_2 from the inner side. Hydrogen peroxide concentration was determined by iodometric titration, whereas water content was determined by the Karl Fischer volumetric method. All kinetic runs were carried out at room temperature.

Selectivity toward H_2O_2 at any time was calculated as follows:

$$S_{H_2O_2} = \frac{[H_2O_2]}{[H_2O_2] + [H_2O]}.$$

3. Results and discussion

3.1. Catalyst characterization

SEM images given in Fig. 1 show the asymmetric structure of the α-Al_2O_3 support. The inside macroporous structure has mean pore size of 3 µm, whereas the external thin layer mean pore size is around 100 nm. Carbon coating is hardly visible in Fig. 1, because carbon did not form an external thick layer, but rather penetrated into the pore structure of the alumina support. Carbon is spread all over the TCM, but mostly deposited in the 100-nm α-Al_2O_3 external layer, where it generates a microporous fine structure. During impregnation and catalytic tests, this microporous structure was filled by capillarity with the solvent.

TEM images of the different samples are shown in Figs. 2a–f. TCM1, containing only Pd, is shown in Figs. 2a and b. In this sample the metal particles are roundish and evenly spread on the amorphous carbon layer. In presence of Pt (TCM3 and TCM4), particles are smaller, irregularly shaped, and grouped in clusters. TCM4 (Figs. 2c, d) shows small particles on carbon and bigger ones near the alumina crystallites. EDS analysis confirmed the presence of both Pd and Pt on