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Palladium-modified catalytic membranes for the direct synthesis of H_2O_2: preparation and performance in aqueous solution

S. Melada [a,*], F. Pinna [a], G. Strukul [a], S. Perathoner [b], G. Centi [b]

[a] *Dipartimento di Chimica, University Ca' Foscari, INSTM Consortium R.U. of Venice, Dorsoduro 2137, 30123 Venice, Italy*
[b] *Dipartimento di Chimica Industriale ed Ingegneria dei Materiali, University of Messina, INSTM Consortium R.U. of Messina, Salita Sperone 31, 98166 Messina, Italy*

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Abstract

A series of new tubular catalytic membranes (TCMs) have been prepared and tested in the direct synthesis of H_2O_2. Such TCMs are carbon-coated asymmetric α-alumina mesoporous membranes supported on macroporous α-alumina. Pd was introduced by deposition–precipitation to obtain an even Pd particle distribution inside the membrane pore network. This type of membrane was active in the direct synthesis of H_2O_2. Catalytic tests were carried out in a semi-batch recirculating reactor under very mild conditions. Concentrations as high as 250–300 ppm H_2O_2 were commonly achieved after 6–7 h on stream, with a particularly high decomposition rate in the presence of H_2. Important features are optimization of the metal deposition procedure and preactivation. To slow down the decomposition and favor the synthesis of H_2O_2, a smooth metal particle surface is needed.

Keywords: Hydrogen peroxide; Direct synthesis; Membrane; Catalytic membrane reactor; Palladium; Heterogeneous catalysis

1. Introduction

Hydrogen peroxide is a commodity that today is almost exclusively produced by the anthraquinone process, developed in Germany in the 1930s [1]. This process is economically feasible only on large-scale plants, and the price of H_2O_2 produced is influenced by the complexity of the process and by the costly separation and concentration steps that are needed. Direct synthesis, which could be a more economic and environmentally acceptable alternative, has been known since the beginning of the 20th century [2], but no industrial application has been found, even given some successful attempts at DuPont during the 1980s [3].

Numerous patents have been filed over the past 30 years dealing with Pd metal or Pd metal alloy (e.g., Pd/X, X = Pt, Au, Ag, Ni) supported catalysts [3–9], homogeneous catalysts [10], electrochemical devices [11], and, only recently, Pd-based monoliths [12], membranes [13,14], and fast flow mixers [15,16].

Only a few related scientific works have been published in the open literature. Most of these describe the use of supported Pd or Pd alloy catalysts [17–22], colloidal Pd clusters [23–26], fuel cells [27], and Au catalysts [28,29] for the direct synthesis of hydrogen peroxide. Among these works, only one paper deals with membranes [30].

Despite the intense patent activity of major chemical companies, no successful industrial application has been claimed. This is because two severe drawbacks must be overcome for the direct synthesis: (1) the formation of explosive H_2/O_2 mixtures that should be avoided and (2) the selectivity of the reaction (whose main product is water) that is still unacceptably low. In principle, the use of specially designed catalytic membranes could overcome both problems [13,14,30].

* Corresponding author.
E-mail address: stefano.melada@unive.it (S. Melada).

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2. Experimental

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 50–100 mg for each tube. The coating was performed by MAST Carbon Ltd., Guildford, UK, and the alumina support was supplied by Hermsdorfer Institut für Technische Keramik, Hermsdorf, Germany.

2.1. Sample preparation

Carbon-coated membranes (CAMs) were activated in CO_2 at 850 °C and then impregnated by a deposition–precipitation method (a classical method to obtain eggshell-type catalysts) optimized during this work [31–33]. This technique consisted of two steps: (1) basification of the membrane surface by soaking in a NaOH solution (0.1 mol) and (2) deposition of $Pd(OH)_2$ by precipitation from an acidic $PdCl_4^{2-}$ solution. The pH of the starting Pd(II) solution changed from 0.7 to 2.7. During impregnation, $Pd(OH)_2$ was deposited into the pore network of the external carbon layer. After Pd deposition, membranes were dried at room temperature, reduced at room temperature in H_2 flow, and washed with distilled water to remove chloride ions. Pd loading was between 1 and 2 wt% with respect to carbon loading.

2.2. Characterization

Membranes were thoroughly characterized by several techniques. Transmission electron microscopy (TEM) images were taken 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). External carbon layers have been scraped away with a knife to give a fine carbon powder. This was suspended in isopropyl alcohol, ultrasonicated for 5–10 min so that the particles were well dispersed and then deposited on a holey carbon film.

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

N_2 physisorption isotherms were determined on small chips of the CAMs. Samples were degassed in vacuo (10^{-2} Torr) and heated at 150 °C for 2 h. N_2 physisorption isotherms were measured at −196 °C on a Micromeritics ASAP 2000 instrument. Specific surface areas were determined by the BET equation in the 0.05–0.2 p/p_0 range. Pore size distributions were calculated with the BJH method.

CO chemisorption measurements were carried out with a pulse technique on a home-made apparatus equipped with a thermostatted reactor and an ESS Genesys quadrupole mass spectrometer interfaced to a computer for data collection and analysis. CO^+ fragments ($m/z = 28$) were used for quantitative measurements. A 1/2 CO/Pd chemisorption stoichiometry was assumed for calculation [34]. 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, all samples were characterized after the catalytic tests. A methanation test showed that CO is removed only above 300 °C. After the methanation step, Pd particles sintered extensively. Before each measurement, Pd was reduced in situ by passing a 5% H_2/He mixture at 25 °C, then thoroughly evacuated with He.

Pd loading was determined by atomic absorption spectroscopy (AAS) from the Pd(II) solutions used for metal deposition on the membranes. Differences between Pd concentration before and after impregnation gave the amount of loaded Pd. The reliability of this analytical method was checked as follows. Pd was extracted from membranes by soaking in boiling HNO_3. AAS determination on dissolved Pd(II) gave the loaded Pd amount. Differences of <3% were obtained by comparing the two analytical methods. Thus differential measurements on Pd solutions enabled determination of the Pd loading without destroying the membrane.

2.3. Catalytic tests

These were carried out in a semi-batch recirculation reactor (Fig. 1), with the membrane sealed in a tubular holder. From the inner side, H_2 was fed at constant pressure (2–5 bar) while an oxygen-saturated acidic solution was continuously circulated on the outer side of the membrane (where Pd was deposited) by means of a peristaltic pump (25 ml/min) equipped with special Tygon® MH tubing. The circulating solution was 100 ml of 0.03 mol H_2SO_4 containing 6 ppm of NaBr. H_2O_2 concentration was determined by permanganometric titration.

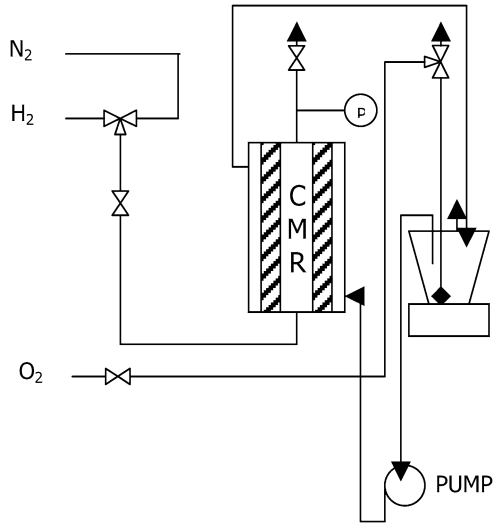

Fig. 1. Scheme of the experimental apparatus used for the catalytic tests.