stirred reaction mixtures were degased under vacuum, and purged three times with argon. Stirring was stopped, and the solutions were allowed to react at room temperature under an anaerobic atmosphere. After 48 h, a 250-µL aliquot was removed, diluted with CH_3CN (750 µL), and sonicated for 7 min to precipitate the CA enzyme. The suspension was centrifuged on an ultrafree-CL-Biomax membrane (PBCC 5000 UFC4 BCC25). This treatment was also applied when no CA was present. The filtrate was lyophilized and redissolved in H_2O/CH_3CN (1:1, 200 µL). The solution was analyzed by reversed-phase HPLC with detection at 230 nm on a Waters 2690 instrument equipped with a Merck RP-Select B reversed-phase column (5 µm, 250 × 4 mm, flow rate: 1 mL min^{-1}). A ternary solvent gradient (solvent A: 0.1 % trifluoroacetic acid in H_2O; solvent B: 0.08 % trifluoroacetic acid in CH_3CN; solvent C: isopropanol) was optimized so that most of the compounds used in this study have different retention times: C: constant at 2 %; B: 0 % during 3 min, then increased to 80 % over 79 min.

The assay described above was optimized to limit side reactions such as disulfide formation, alkyl chloride hydrolysis, and trialkyl sulfonium formations. Some of these side products have been identified on the chromatograms and are mentioned below. The products **3a**–**e** were synthesized and characterized separately to validate their assignments on the chromatograms.

The following retention times and absorption coefficients were measured: **3a** (10 min, $\varepsilon_{230} = 12000\ \text{cm}^{-1}\text{M}^{-1}$), **3b** (20 min, $\varepsilon_{230} = 16000\ \text{cm}^{-1}\text{M}^{-1}$), **3c** (33 min, $\varepsilon_{230} = 15000\ \text{cm}^{-1}\text{M}^{-1}$), **3d** (57 min, $\varepsilon_{230} = 23000\ \text{cm}^{-1}\text{M}^{-1}$), **3e** (57 min, $\varepsilon_{230} = 23000\ \text{cm}^{-1}\text{M}^{-1}$), **2d** (40 min), **2e** (40 min), 4-hydroxymethylbenzoic acid (14 min), 3-hydroxymethyl benzoic acid (14 min), benzoic acid (22 min), α,α-tosylamide disulfide (61 min, $\varepsilon_{230} = 23000\ \text{cm}^{-1}\text{M}^{-1}$).

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Nonhazardous Direct Oxidation of Hydrogen to Hydrogen Peroxide Using a Novel Membrane Catalyst

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Hydrogen peroxide is a clean oxidizing agent that is useful for converting organic compounds into value-added products (bulk and fine chemicals), as well as for industrial and municipal waste-water treatment, and water disinfection. However, because of the high cost of its production by the standard anthraquinone process,[1] hydrogen peroxide cannot be used for the production of bulk organic chemicals or for water treatments. Moreover, the anthraquinone method is not a green process. Hence, it is of great practical importance to develop an environmentally friendly process based on the direct oxidation of hydrogen to hydrogen peroxide. Although the formation of hydrogen peroxide in the palladium-catalyzed liquid-phase oxidation of hydrogen has been known since 1914, and several patents have been issued since then,[2–11] this process could not be put into practice. This is mostly because of its highly hazardous nature (the explosive limits of hydrogen/oxygen gas mixtures are very wide and are further widened with increasing pressure), and/or poor

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hydrogen peroxide selectivity and yield. The readily available literature on this process is scarce, and the conversions and selectivities reported earlier are poor (maximum 8.7% H_2O_2 selectivity with 41% H_2 conversion at 0.65 MPa).[12]

Our new approach, which gives a very high conversion (up to 100%) with high H_2O_2 selectivity, involves the liquid-phase oxidation of H_2 by O_2, without any explosion hazards: a) a composite Pd-membrane catalyst (Figure 1a) was specially designed to greatly increase the H_2O_2 selectivity, and b) the H_2 is separated from the O_2 in the liquid reaction medium in the reactor by the membrane catalyst, thereby avoiding the formation of an explosive gas mixture (Figure 1b).

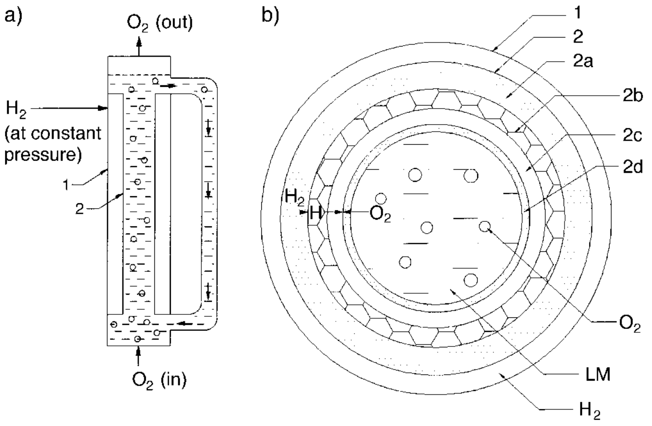

Figure 1. Schematic representation of the composite Pd-membrane catalyst and the membrane reactor for the nonhazardous oxidation of H_2 by O_2 to H_2O_2. a) Membrane loop reactor with recirculation of the liquid medium (0.02 M H_2SO_4) by gas lift. b) Cross sectional view (not to scale) of the membrane reactor and the membrane catalyst (1 = membrane reactor wall, 2 = tubular membrane catalyst, 2a = tubular membrane support with α- or γ-alumina (200 nm) deposited on the inner walls, 2b = Pd–Ag alloy film on the α- or γ-alumina, 2c = Pd film (on the Pd–Ag alloy) with or without oxidation by N_2O or H_2O_2, 2d = hydrophobic polymer membrane permeable to gases and vapours, LM = liquid medium (0.02 M H_2SO_4); area of the metallic membrane = 50 cm^2).

We have observed a large increase in the H_2O_2 selectivity as a result of the deposition of a thin film of pure palladium on a stable Pd–Ag alloy/γ- or α-alumina membrane. The selectivity is increased markedly by the bulk oxidation of the Pd film. The deposition of a thin film of a hydrophobic polymer membrane on the oxidized Pd film also causes a further small increase in the selectivity. In the Pd-based membrane reactor, H_2 gas (at constant pressure) is separated by the membrane catalyst from the aqueous liquid medium (0.02 M H_2SO_4) through which O_2 gas is bubbled (Figure 1). Because of its permselectivity, only hydrogen atoms permeate through the Pd-based metallic membrane.[13–16] At the surface of the Pd film or of the oxidized Pd film, the hydrogen atoms react with the oxygen molecules transported in the liquid medium, to form H_2O_2:

$$\mathrm{H + O{-}O + H \rightarrow H{-}O{-}O{-}H} \tag{1}$$

Because of its high affinity for water, the H_2O_2 formed in this reaction [Eq. (1)] is absorbed by the aqueous liquid medium, which is recirculated over the surface of membrane catalyst in the membrane loop reactor by the gas lift (Figure 1a).

To illustrate this approach, H_2 was oxidized by treating it with O_2 in the liquid reaction medium (0.02 M H_2SO_4). A novel composite Pd-based membrane catalyst (Figure 1a) was used at different stages of its preparation, in a membrane loop reactor (Figure 1b). We also used powdered Pd-containing catalysts (with or without Ag), and a mixed H_2 and O_2 gaseous feed in a three-phase stirred reactor. We then studied the decomposition of H_2O_2 over the powdered catalysts, which were stirred in the reactor.

The results of the oxidation of H_2 to H_2O_2 using the three different membrane catalysts at the different stages of their preparation are presented in Figure 2. The membrane catalyst

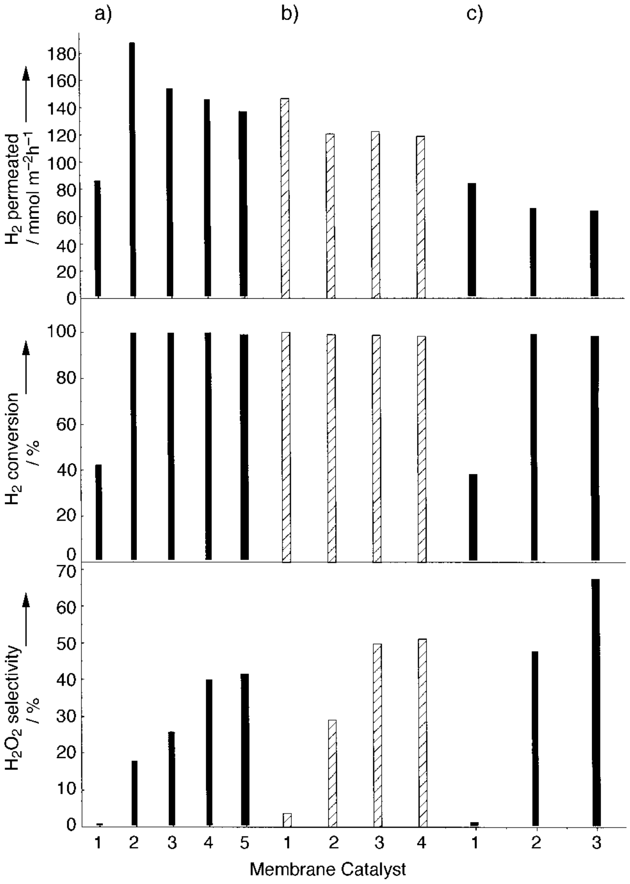

Figure 2. Beneficial effect on the H_2O_2 selectivity of: the deposition of a thin Pd film on Pd–Ag alloy membrane (deposited on α- or γ-alumina membrane support), the oxidation of the Pd film, and the deposition of a thin hydrophobic polymer membrane on the oxidized Pd film, in the oxidation of H_2 at 29°C (H_2 pressure 243 kPa, O_2 pressure 101 kPa). 1a) Pd–Ag alloy (26.5 wt% Ag, 173.1 $g\,m^{-2}$) deposited on an α-alumina membrane support, 2a) after deposition of a Pd film (0.6 μm) on the alloy, 3a) after increasing the thickness of the Pd film from 0.6 to 1.4 μm, 4a) after oxidation of the Pd film by N_2O at 250°C for 2 h and 5a) after deposition of a thin film 0.9 μm of silicon rubber on the oxidized Pd film; 1b) for Pd–Ag alloy (10.1 wt% Ag) alloy (36.2 $g\,m^{-2}$, film thickness 3.3 μm (max)) deposited on γ-alumina membrane support, 2b) after deposition of Pd film (0.8 μm) on the alloy, 3b) after oxidation of the Pd film by N_2O at 250°C for 2 h, 4b) after deposition of a thin film (0.5 μm) of polyether sulfone polymer membrane on the oxidized Pd film; 1c) for Pd–Ag (30.5 wt% Ag) alloy (54.2 $g\,cm^{-2}$, film thickness 4.9 μm (max)) deposited on γ-alumina membrane support, 2c) after deposition of the Pd film (1.5 μm) on the alloy, 3c) after oxidation of the Pd film with concentrated H_2O_2 (30% aqueous H_2O_2) at 80°C for 2 h. Concentration of H_2O_2 in the liquid medium after 3 h (mmol dm^{-3}): 1a) 0.09, 2a) 7.9, 3a) 9.9, 4a) 13.4, 5a) 13.5, 1b) 0.4, 2b) 8.4, 3b) 14.8, 4b) 15.6, 1c) 0.08, 2c) 8.5 and 3c) 12.3.

that contained only Pd (i.e. no Ag) lost its permselectivity for H_2 as a result of the pinholes that developed in the Pd membrane because of the formation of a brittle β-Pd hydride phase.[17]

For comparison, H_2 was oxidized to H_2O_2 by using a mixed H_2 and O_2 gaseous feed. The H_2O_2 was also decomposed over Pd–Ag/γ-alumina, Pd/γ-alumina, and oxidized Pd/γ-alumina catalysts in a stirred slurry reactor at 29 °C (Figure 3). X-ray diffraction studies of the oxidized Pd/γ-alumina showed the presence of a PdO phase as well as a metallic Pd phase, which indicated a partial bulk oxidation of the Pd catalyst in its treatment with N_2O or H_2O_2.

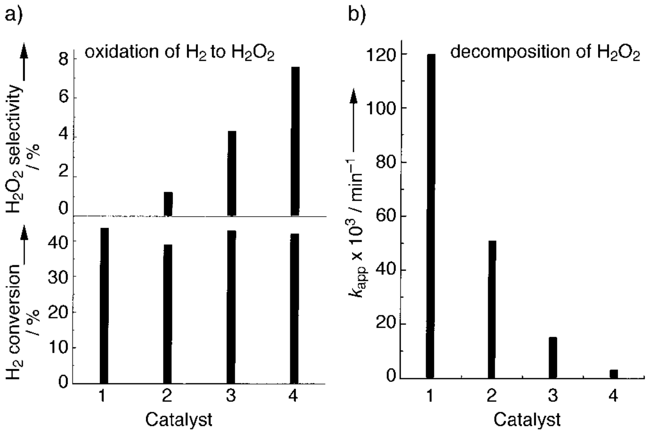

Figure 3. Results of a) direct oxidation of H_2 by O_2 to H_2O_2 by using a mixed H_2 and O_2 gas feed (1.7 vol% H_2 in O_2) and b) decomposition of H_2O_2 over the powdered Pd–Ag alloy (25 wt% Ag)/γ-alumina (6.3 wt%; 1a and 1b), Pd/γ-Al_2O_3 (5 wt%; 2a and 2b), oxidized (with N_2O) Pd/γ-Al_2O_3 (5 wt%; 3a and 3b), and oxidized (with H_2O_2) Pd/γ-Al_2O_3 (5 wt%; 4a and 4b) catalysts, stirred in a slurry reactor at 29 °C, with H_2SO_4 (0.02 M) as the reaction medium (k_a = apparent first-order rate constant).

Based on the results in Figure 2, the following observations were made: a) the membrane catalyst that contained only Pd–Ag alloy shows little or no selectivity for H_2O_2 formation; b) the H_2O_2 selectivity is greatly increased after the deposition of a Pd film, depending on its thickness; c) the H_2O_2 selectivity is increased appreciably if the Pd film is oxidized; d) the deposition of a hydrophobic polymer membrane on the oxidized Pd film also causes a further small increase in the H_2O_2 selectivity. These observations for the membrane reactor are consistent with those for the slurry reactor, which uses a similar catalyst in the form of fine particles, and a mixed feed of H_2 and O_2 gases (Figure 3a).

The reactions involved in the low temperature (25 °C) Pd-catalyzed oxidation of H_2 are:

$$H_2 + O_2 \longrightarrow H_2O_2\ (\Delta H = -135.9\ \mathrm{kJ\,mol^{-1}}) \quad (2)$$

$$H_2 + 0.5\,O_2 \longrightarrow H_2O\ (\Delta H = -241.6\ \mathrm{kJ\,mol^{-1}}) \quad (3)$$

$$H_2O_2 \longrightarrow H_2O + 0.5\,O_2\ (\Delta H = -105.8\ \mathrm{kJ\,mol^{-1}}) \quad (4)$$

$$H_2O_2 + H_2 \longrightarrow 2\,H_2O\ (\Delta H = -211.5\ \mathrm{kJ\,mol^{-1}}) \quad (5)$$

These reactions are exothermic and thermodynamically feasible over a wide temperature range. However, the oxidation of H_2 to H_2O_2 [Eq. (1)] is favored at lower temperatures and higher pressures, whereas the conversion of H_2O_2 [Eq. (4) and (5)] occurs more readily at higher temperatures. Therefore, the formation of H_2O_2 is preferred at lower temperatures and higher pressures.

Little or no H_2O_2 selectivity was observed for the Pd–Ag alloy, which can be attributed to its high H_2O_2 conversion activity. The H_2O_2 decomposition activity of the Pd-containing catalysts was found to be in the following order: Pd–Ag > Pd > Pd–PdO (Figure 3b). The observed H_2O_2 selectivity trend for both the membrane and slurry catalysts (Figure 2 and 3a) is consistent with this order; the lower the H_2O_2 decomposition activity, the higher the H_2O_2 selectivity. The role of the hydrophobic polymer membrane is to increase the H_2O_2 selectivity by avoiding catalytic conversion of H_2O_2 [Eq. (4) and (5)], once it is formed and absorbed by the aqueous liquid medium. The hydrophobic polymer membrane provides a barrier for returning the H_2O_2 back to the catalyst surface.

Both the selectivity and the H_2 conversion are much higher for the membrane catalyst than for the corresponding catalyst used in the slurry reactor with a mixed feed of H_2 and O_2 gases (Figure 2 and 3a). Furthermore, the H_2O_2 selectivity of the membrane catalyst (Figure 2) is much higher than that of similar Pd-containing catalysts that use a mixed feed of H_2 and O_2 gases (Figure 3a), and even at much higher pressure (>2 MPa).[12] The higher selectivity and conversion can be attributed mostly to the formation of H_2O_2 by the reaction of the permeated hydrogen atoms (which are more reactive than H_2 molecules) with molecular O_2 [Eq. (1)] at the catalyst surface, in the membrane process. Once the H_2O_2 is formed and absorbed by the liquid medium, its conversion is eliminated or decreased by providing a resistance for the transport of H_2O_2 back to the catalyst surface using the polymer membrane. Also, since the conversion of H_2 is complete or close to 100%, there is no need for the separation of unconverted H_2 from the reactor effluent gas (unconverted O_2) before it is recycled in the process. The concentration of H_2O_2 in the liquid medium could be increased by increasing the reaction time and/or the H_2 pressure, while maintaining the pressure drop across the membrane catalyst well below its burst pressure. A further improvement in the selectivity by optimizing the design of the membrane catalyst and the process conditions, and also by operating the process at much higher pressures would make this environmentally friendly process much more attractive and also commercially more feasible.

Experimental Section

Pd–Ag alloy was deposited on the inner walls of an α-alumina (pore size = 200 nm) or a γ-alumina (2 nm) membrane support tube (i.d. 7 mm, o.d. 10 mm and length 250 mm; Scoete des Ceramiques Technique, France), by the electroless deposition technique described elsewhere.[17, 18] The Pd film on the Pd–Ag alloy was also deposited by the same technique. The Pd film was oxidized by N_2O at 250 °C for 2 h, or by a solution of H_2O_2 (30%) at 80 °C for 2 h. The hydrophobic polymer membrane on the oxidized Pd film was deposited by exposing it to a polymer solution (silicone rubber (polydimethyl siloxane)) and a cross-linking agent, trimethylol propane ($C_2H_5C(CH_2OH)_3$) dissolved in toluene or polyether sulfone dissolved in *N,N*-dimethylformamide, and drying in air at 80 °C for 2 h. The Pd–Ag alloy (25 wt% Ag)/γ-alumina (6.3 wt%) was prepared by impregnating the Pd/γ-alumina catalyst (5 wt%, powder, Lancaster Chemicals, England) with silver nitrate and calcining at 500°C for 4 h under helium. The oxidation of H_2 in the membrane loop reactor was carried out batchwise with respect to H_2 and liquid medium (0.02 M aqueous H_2SO_4) and continuous with respect to O_2 (50 $cm^3 min^{-1}$) for a period of 3 h (Figure 1 a). The liquid medium (60 cm^3) was recirculated continuously by the gas lift mechanism. On the other hand, the H_2 was oxidized by O_2 over the magnetically stirred powdered catalysts in a glass slurry reactor (capacity 250 cm^3) at atmospheric pressure (101 kPa), by using a mixed feed of H_2 and O_2 (1.7 vol% H_2) and H_2SO_4 (150 cm^3, 0.02 M) as the reaction medium. In both cases, the H_2O_2 formed in the reaction was determined by iodometric analysis. The concentration of H_2 in the reactor effluent gases was measured by an online H_2 analyzer. The amount of H_2 that permeated through the membrane catalyst was measured from a decrease in the pressure in the H_2 reservoir, from which the H_2 was supplied to the membrane reactor at a constant pressure. The H_2O_2 was decomposed over the powdered catalysts (0.2 g) by stirring in aqueous H_2SO_4 (105 cm^3, 0.02 M) in the glass reactor; the initial concentration of H_2O_2 in the medium was 0.3 wt%.

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Crystal Structure of Potassium Croconate Dihydrate, after 175 Years

Jack D. Dunitz,* Paul Seiler, and Werngard Czechtizky

Potassium croconate dihydrate, $K_2(C_5O_5) \cdot 2H_2O$, was isolated by Leopold Gmelin in 1824 and described as an orange-colored (*pomeranzenfarbige*) crystalline hydrate in 1825.[1] Obtained by heating a mixture of potash and carbon and predating Wöhler's urea synthesis by three years, it thus has a claim to be the first "organic" compound to have been synthesized from inorganic precursors (for an account of early work on oxocarbon compounds, see the chapter by West.[2]) Although some X-ray studies have been reported on other crystalline croconate salts (e.g., ammonium croconate,[3] diethylammonium croconate,[4] ammonium hydrogencroconate,[5] and rubidium hydrogencroconate[5]), the structure of the potassium salt has remained unknown until now.

We have obtained the substance by slow evaporation of an aqueous solution of commercial potassium rhodizonate $K_2(C_6O_6)$[6] in air. This gave a mixture of colorless and orange-yellow needles, of which the former could be identified as potassium oxalate monohydrate,[7] while the latter was shown by X-ray analysis to be potassium croconate dihydrate,[8] both presumably derived from air oxidation of the rhodizonate. Apart from its historical interest, the crystal structure has some noteworthy features. It gives the first reasonably precise dimensions of the aromatic ring system and shows a remarkable stacking of the planar, doubly negatively charged croconate anions.

From the dimensions of the croconate dianion shown in Figure 1, it is evident that it does not deviate much from fivefold symmetry in the crystal environment. The slight differences among the individual distances may be real and attributable to the lower symmetry of the crystal environ-

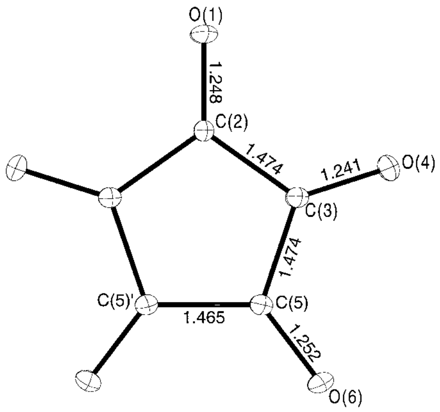

Figure 1. Bond lengths [Å] in the croconate dianion of $K_2(C_5O_5) \cdot 2H_2O$ (estimated standard deviations are ca. 0.003 Å). The dianion has crystallographic C_2 symmetry. The oxygen atoms deviate by up to 0.076 Å from the mean plane of the carbon skeleton (planar to within 0.025 Å). The C-C-C angles are all within 0.5° of 108°, and the C-C-O angles all within 1° of 126°.

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