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Porous Pd-Containing Polypropylene Membranes for Catalytic Water Deoxygenation

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Abstract—Water deoxygenation has been studied in a catalytic membrane reactor in which oxygen is reduced with hydrogen fed into the hollow fiber of a porous polypropylene membrane containing palladium metal on its outer surface. Palladized fibers obtained by different methods and the initial fibers have been characterized by dynamic desorption porosimetry, gas permeability measurements, X-ray structure determination, and light microscopy. The possibility of efficient water deoxygenation at room temperature is demonstrated.

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Deoxygenation is an important step in the preparation of high-quality industrial water for a wide variety of commercial-scale processes. Ultrapure water is used in various industries, including heat power plants (boilers), food industries (beer making), microelectronics (semiconductor fabrication), and oil and gas industries (as injection water). The present-day industries impose stringent requirements on the concentration of dissolved oxygen in process water. The equilibrium oxygen concentration in water under normal conditions is 8 ppm. Many industries require that this concentration should be reduced by 2–3 orders of magnitude. The oxygen concentration in ultrapure water for microelectronics should not exceed 1 ppb.

There are physical, chemical, and catalytic methods for water deoxygenation, and all of them have drawbacks. Physical deoxygenation methods, such as vacuum degassing and the inert-gas scavenging of oxygen, are incapable of reducing oxygen to the desired level [1–4]. Furthermore, the physical methods are very energy-intensive. Chemical methods employ reducing agents (hydrazine hydrate, sulfites) contaminating both the environment and the water being purified [5]. The most effective modern methods for water ultrapurification are based on the reduction of dissolved oxygen with hydrogen on a palladium catalyst. The present-day catalytic methods include two steps, specifically, hydrogen dissolution in water followed by oxygen reduction on a palladium catalyst.

In 1972, Academician Gryaznov and his colleagues discovered the phenomenon of reaction conjugation on membrane catalysts based on palladium and its alloys [6]. Gryaznov's laboratory studied hydrogenation and dehydrogenation reactions in which hydrogen was fed or removed through a solid palladium alloy membrane. Such membranes served as the prototype for the first membrane reactors [7]. The membrane reactor is an apparatus integrating membrane separation and a chemical reaction into a single technology. There are different variants of this integrated technology [8].

Here, we suggest a new type of water deoxygenation membrane catalyst, specifically, a porous, hydrophobic, polypropylene, hollow-fiber membrane with palladium supported on the outer surface of the fibers. The reducing agent is hydrogen, which is fed inside the fibers and diffuses through pores to the outer, Pd-coated, side of the fibers to reduce oxygen dissolved in water.

EXPERIMENTAL

Initial Membranes

The initial membranes were Accurel Q3/2 (outer diameter, 1mm; wall thickness, 0.2 mm; average pore diameter, 0.265 μm; 79% porosity), manufactured by Membrana GmbH, Germany.

Preparation of Membrane Catalysts

Two methods were used in the chemical deposition of palladium onto the outer surface of the porous polypropylene hollow-fiber membranes.

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† Deceased.

Table 1. Properties of the Pd-containing porous polypropylene membranes

Membrane	Palladizing method	Palladium content of the membrane surface, wt %	N_2 permeability, $cm^3/(cm^2$ s atm)	Unit cell parameter of Pd, Å
M-0	–	0	2.7	–
M-1	I	24	2.2	3.893
M-2	II	0.73	–	3.904
M-3	II	0.68	2.7	3.891
M-4	II	0.60	–	3.891
M-5	II	0.30	–	3.891

In order to achieve the strongest possible and uniform adhesion between the metal and the polymer, the membrane surface was roughened by etching with a mixture of mineral acids. In the first deposition method (method I), tetramminepalladium chloride was reduced with hydrazine hydrate in aqueous ammonia [9, 10]. This method afforded membranes containing >20 wt % Pd on their outer surface. In the second method (method II), $PdCl_2$ was reduced with an aliphatic alcohol, which served both as the reducing agent and as the solvent [11]. This method afforded membranes containing 0.3–0.73 wt % Pd on their outer surface. The properties of the membranes obtained by these two methods are listed in Table 1.

Supported palladium was quantified by atomic absorption spectroscopy on an AAS-30 Carl Zeiss Jena spectrometer.

Characterization of the Catalytic Membranes

The initial and catalytic Pd-containing membranes were characterized by dynamic desorption porosimetry, gas permeability measurements, X-ray structure determination, and light microscopy.

Dynamic desorption porosimetry. The porous structure of the membranes was studied using the dynamic desorption porosimetry technique described in our earlier publications [12–14]. The adsorbate was cyclohexane. Measurements were taken at a constant temperature of 30°C.

Gas permeability measurements. The gas permeability of the initial and catalytic membranes was measured at room temperature using a setup designed for flat and hollow-fiber membranes [15]. The permeating gas was pure N_2.

X-ray structure determination. The X-ray diffraction study of the palladium catalysts was carried out on a D-8 (Bruker) diffractometer using CuK_α radiation filtered with a graphite monochromator placed in the reflected beam. The samples were examined in a 2θ range of 10°–90° with $2\theta = 0.02°$ increments. The count time per point was 10–50 s. Diffraction patterns were processed using the Origin and PCW-2.4 programs [16]. Standard data for palladium metal were taken from the diffraction database PC PDF Win 2000, set 46-1043 (space group $Fm3m$, $a = 3.890$ Å).

Electron microscopy. An M-2 membrane, cooled in liquid nitrogen, was examined under a Jeol microscope operating in the backscattering mode at 200× magnification.

Light microscopy. The initial and palladized membranes were examined under a large inverted reflection photomicroscope (Neophot 30).

Catalytic Membrane Reactor

The experimental setup for investigating water deoxygenation in the membrane contactor reactor is schematized in Fig. 1. The hollow fibers, 22 cm in length, were bundled, and both ends of the bundle were sealed in a glass collector using a silicone sealant. The membrane was mounted in a 70-ml batch reactor, which was filled with distilled water. The working surface area of the membrane was taken to be equal to its

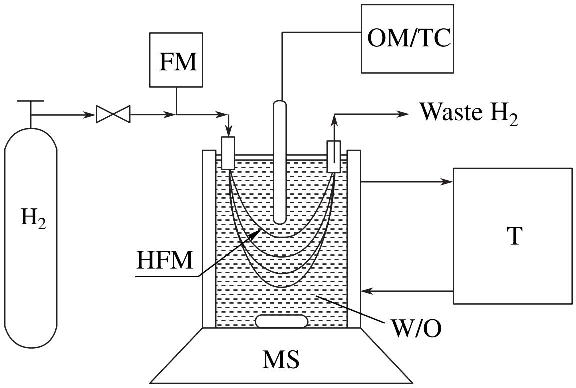

Fig. 1. Schematic of the setup for water deoxygenation in a stationary open-air reactor: H_2 = hydrogen cylinder, FM = flowmeter, HFM = catalytic hollow-fiber membrane, MS = magnetic stirrer, OM = oximeter, TC = thermocouple, T = thermostat, and W/O = water containing dissolved oxygen.

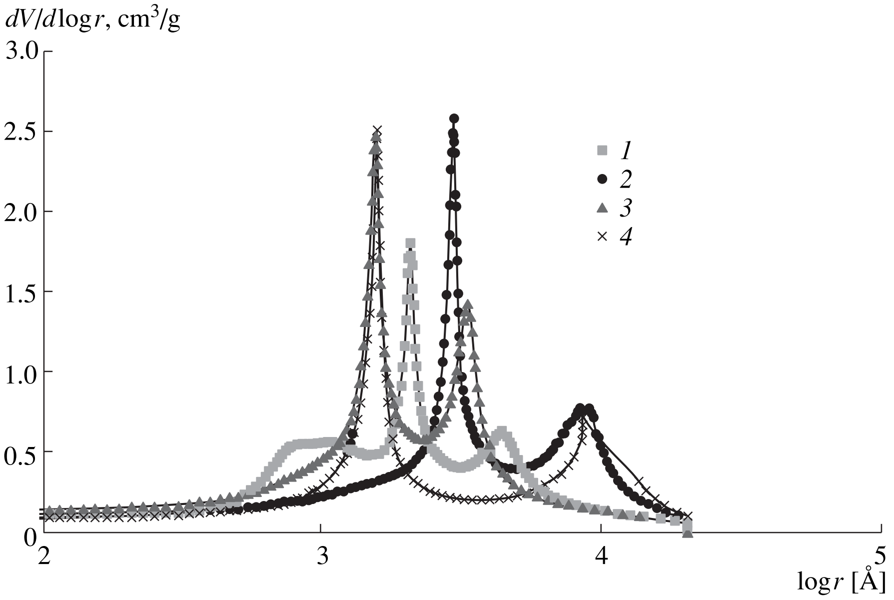

Fig. 2. Pore-size distribution function: (*1*) M-0; (*2*) etched membrane; (*3*) M-3 (0.68 wt % Pd), and (*4*) M-1 (24 wt % Pd).

geometrical surface area. The water in the reactor was stirred with a magnetic stirrer (600 rpm). The water temperature was maintained constant in each run using a water thermostat. Deoxygenation was studied at T = 288–318 K. After the preset temperature was established in the reactor, hydrogen (6 ml/min) was fed into the hollow-fiber membrane. The oxygen concentration in water was measured with an Oxi 3301 oximeter, whose sensor was mounted inside the reactor. The sensor was equipped with a thermocouple, so it was possible to measure the oxygen concentration in water and the reactor temperature simultaneously.

RESULTS AND DISCUSSION

Properties of the Membranes

The initial membrane was white. After the outer surface of the fibers was palladized, the membrane turned dark gray. The inner surfaces and cross sections of the fibers remained white throughout the membrane thickness. Therefore, all of the palladium was localized on the outer surfaces of the fibers and did not penetrate into the pores.

The initial, etched, and Pd-containing membranes were examined by dynamic desorption porosimetry, and differential pore-size distribution curves were obtained (Fig. 2). The membranes have two dominant pore sizes. The initial membrane M-0 (curve *1*) differs from the three other membranes in that it contains pores smaller than 100 nm. The left peak for the initial membrane, which occurs at log r = 3, is apparently assignable to transport pores (that is, larger pores present in the fiber are connected with the surface through smaller, transport, pores). The size of transport pores measured for the initial membrane is in agreement with the membrane's certificate. This is indirect evidence that our measurements are correct. Furthermore, there are two well-defined peaks near 200 and 500 nm. These peaks survive all processing stages, but their positions and the corresponding pore volumes change. After etching (curve *2*), the peak characterizing the smallest pores is not observed. The two other peaks are shifted to larger pore radii of about 300 and 900 nm, and the corresponding pore volumes are markedly larger.

Slight palladization (0.68 wt % Pd, curve *3*) causes a substantial decrease in the dominant pore radius, shifting the strongest peak from 300 to 155 nm, and does not exert any significant effect on the largest pores with a radius of ~900 nm. The total pore volume remains the same as in the etched membrane (curve *2*). The porosity of the palladized membrane is 81%. It can be assumed that even a small amount of palladium fixes the loose membrane structure resulting from etching without significantly reducing the pore volume. In this case, palladium serves as a structure-forming element (framework) and does not fill the pore space.

The introduction of a large amount of palladium causes a decrease in the size of the largest pores (curve *4*). It is possible that the new peak corresponds to the structures formed by pores and palladium particles located near their mouths. The position of the strongest peak remains almost the same; therefore, the corresponding pores are inaccessible to palladium particles. Furthermore, palladium particles form a framework structure with a pore radius of <100 nm (curve *3* is above curve *4* in this region). As a consequence, the M-1 membrane is slightly more porous than the M-3 membrane. For M-1, the dominant pore radius is 151 nm and porosity is 84%.

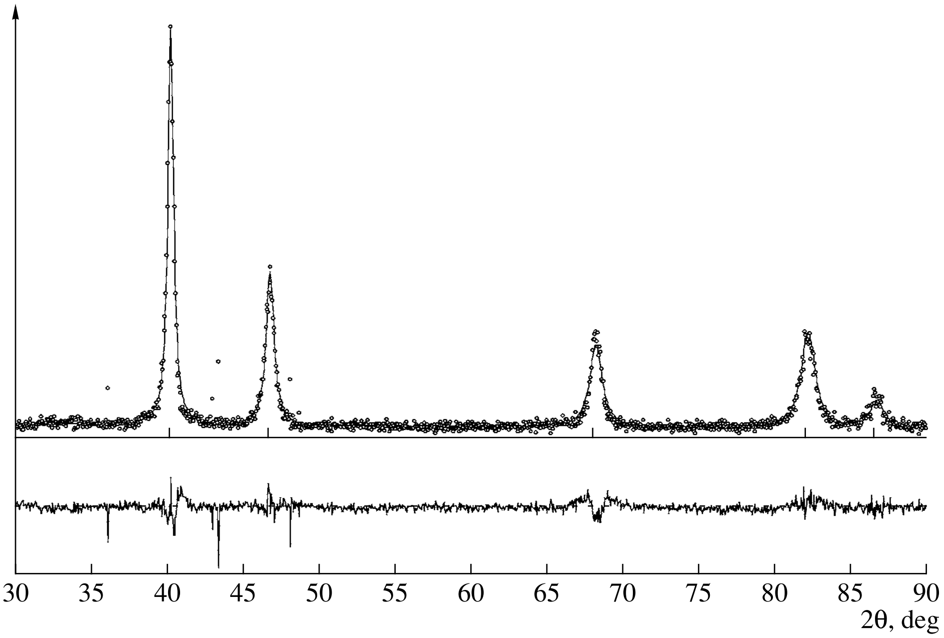

Fig. 3. X-ray diffraction data: the points represent the experimental diffraction pattern from M-1 (24 wt % Pd), and the solid line is the diffraction pattern calculated for Pd using the PCW 2.4 program. Below is the difference curve. The divergence factor is $R = 0.12$.

Table 1 lists N_2 permeability data for the initial and Pd-containing membranes. Evidently, the polypropylene hollow-fiber membrane palladized by method II (M-3) has the same gas permeability as the initial membrane. The membrane palladized by method I (M-1) is ~20% less permeable than the initial membrane. This is evidence of a decrease in the pore size. It is likely that palladium particles partially block the small pores.

X-ray diffraction data are presented in Table 1. The accuracy of the lattice constant measurements is not high because of difficulties in focusing the X-ray beam on the tubular surface of the sample and because of the small amounts of Pd in the membranes M-2–M-5 (Table 1). The error in the unit cell parameter is $\Delta a = \pm 0.001$ Å for M-1 and $\Delta a = 0.005$–0.01 Å for M-2–M-5.

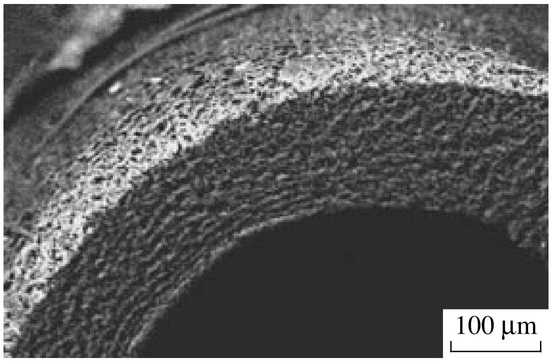

Fig. 4. Electron micrograph of the cross section of the M-2 membrane (0.73 wt % Pd).

Compare the experimental diffraction pattern from M-1 with the theoretical diffraction pattern calculated for Pd using the PCW 2.4 program (Fig. 3). In the 2θ range between 30° and 90°, all reflections are due to the crystal structure of palladium. The unit cell parameter of Pd refined using these data is somewhat larger than the parameters presented in Table 1.The diffraction pattern does not indicate the presence of any other Pd-containing phases (e.g., palladium oxides).

Figure 4 shows an electron micrograph obtained using the backscattering technique for the cross section of the catalytic membrane M-2. The palladium layer appears as a light area on the outer surface of the fiber (in the upper left-hand corner of the micrograph) [17].

The initial and catalytic membranes were examined under a light microscope at 500× magnification (Fig. 5). The microscope automatically optimized the exposure time to obtain a better image. The exposure time was the longest (~1 min) for the M-0 membrane (Fig. 5a) and the shortest (~1–2 s) for the M-1 membrane (Fig. 5c), which contained 24 wt % Pd. The dark fields in these micrographs are the outer mouths of membrane pores, and the white fields are the images of palladium on the membrane surface. Clearly, the larger the amount of palladium on the fiber surface, the higher the contrast of the image of the porous surface.

Water Deoxygenation

Table 2 presents the characteristics of the palladized polypropylene hollow-fiber reactors that were used in this water deoxygenation study (Fig. 1).

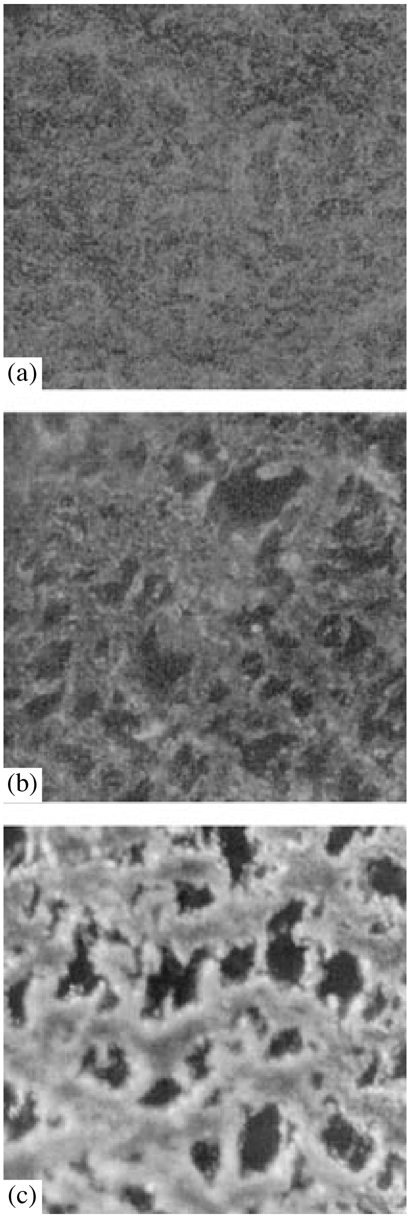

Fig. 5. Optical micrographs of the outer surface of the membranes (a) M-0, (b) M-3 (0.68 wt % Pd), and (c) M-1 (24 wt % Pd). Magnification: 500×.

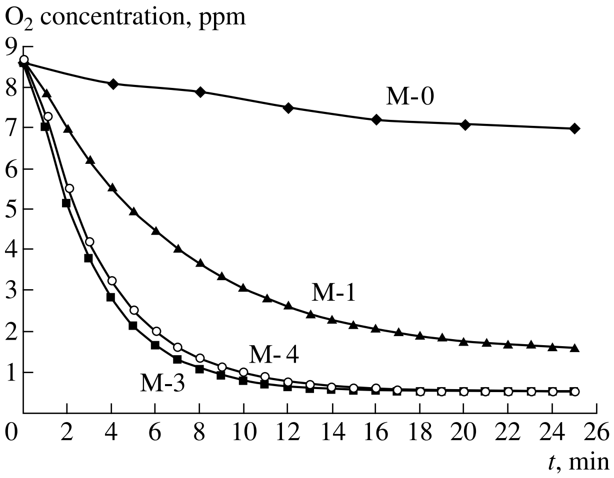

Fig. 6. Oxygen concentration in water as a function of deoxygenation time ($T = 295$ K).

An investigation of the effect of temperature (288–318 K) on the water deoxygenation rate has demonstrated that raising the temperature by 30 K accelerates deoxygenation by a factor of ~3.

Figure 6 plots the concentration of dissolved oxygen versus deoxygenation time at 295 K. In the reactor using the initial membrane (R-1), the oxygen concentration decreased only slightly with time. This trend can be explained in terms of the physical scavenging of dissolved oxygen by hydrogen. As compared to R-1, the reactors with a Pd-containing catalytic membrane afforded water with a >75% lower oxygen concentration. This increase in the deoxygenation efficiency is due to the joint effect of physical scavenging and the catalytic reduction of oxygen with hydrogen.

In the reactor R-4, which consists of membranes containing 24 wt % Pd, the palladium deposit is made up of 100-nm to 1-μm crystals (according to SEM data). In the reactors R-2 and R-3, which consist of catalytic membranes containing <1 wt % Pd, the palladium crystal size is 100–200 nm. Comparing the performances of the reactors R-2, R-3, and R-4 has demonstrated that the extent of deoxygenation depends not only on the amount of deposited palladium but also on the catalyst/water contact area, which is determined by the number of membranes in the reactor. Therefore, it is appropriate to use membranes in which the amount of palladium is a few percent, the surface is uniformly metallized, and all of the palladium is involved in the reduction of oxygen with hydrogen.

The curves plotted in Fig. 6 flatten out because the process was carried out in open-air reactors. For each reactor, the oxygen concentration reaches some steady-state value determined by the water deoxygenation rate

Table 2. Characteristics of the catalytic membrane reactors

Reactor	Membrane	Membrane surface area, cm^2	O_2 concentration*, ppm
R-1	M-0	28	7.10
R-2	M-4	72.5	0.57
R-3	M-3	72.5	0.55
R-4	M-1	24	0.76

* The concentration of dissolved oxygen in the 20th minute of the run.

and by the dissolution rate of oxygen from the air over the water surface.

CONCLUSIONS

We have obtained porous, palladized, polypropylene, hollow-fiber membranes. The palladium content of these membranes depends on the chemical deposition method (method I, 24 wt % Pd; method II, 0.3–0.73 wt % Pd).

The palladizing of the outer surface of polypropylene fibers using method II minimizes both the mass-transfer resistance and the amounts of palladium and hydrogen necessary for efficient water deoxygenation.

It has been demonstrated by X-ray diffraction that the palladium deposit on the outer surface of a polypropylene fiber is crystalline and does not contain any other Pd-containing phases.

With the palladized, porous, polypropylene, hollow-fiber membranes described here, water deoxygenation with hydrogen fed into the hollow fibers can be carried out at room temperature.

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