

Synthesis and Morphology of Platinum-Coated Hollow-Fiber Carbon Membranes

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ABSTRACT: Hollow-fiber carbon membranes were prepared and used as support media for a platinum catalyst. The platinum metal was deposited onto the surface of the hollow-fiber carbon membranes by three different techniques: solution coating with chloroplatinic acid, which is the commonly used technique; vapor deposition, involving the sublimation of the platinum metal; and magnetron sputter coating, the most effective method. The hollow-fiber carbon membranes coated with a chloroplatinic acid solution were studied with scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDAX). The platinum coating grew on the surface, unevenly, in the form of small crystals. The percentage of platinum on the surface was too low to be detected by EDAX. The high-vacuum evaporation coating of the membranes with platinum was also studied with both SEM and EDAX. Again, because of the low percentage of platinum, EDAX did not reveal any platinum on the surfaces of the membranes. The magnetron sputter coat-

ing of platinum onto the membranes was performed and studied with SEM. The thickness of the coated platinum could be varied through variations in the coating time. The cavities observed in the micrographs were formed during the coating operations by the presence of dust particles on the membranes. An SEM micrograph of a hollow-fiber carbon membrane, produced from a polyacrylonitrile-based precursor, spun with a low amount of dimethyl sulfoxide in the bore fluid, and coated with platinum, showed a skin on the outside and a porous elongated structure inside the skin. The distance between the inner and outer skins contained fingerlike pores of various sizes. The largest pores were found near the inside skin, whereas the smallest pores were next to the outside skin. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1051–1058, 2003

Key words: fibers; membranes; catalysts

INTRODUCTION

The use of platinum metal as a catalyst has been studied since the early 1960s. Several workers studied the fundamentals of creating platinum catalysts on α -alumina;^{1–13} Pt–U, Pt–Ir, Pt–Rh, and Pt–Re on γ -alumina;¹² Pt–Sn/Al₂O₃ (tin/alumina);¹⁴ Pt–Ga/Al₂O₃ (germanium/ γ -alumina);¹⁵ Pt–NaCs β (sodium/cesium);¹⁶ Pt–WO₃/ZrO₂ (tungsten/zirconium);¹⁷ and other support systems such as gadolinium.¹⁸ One of the properties that greatly affects the performance of heterogeneous catalysts is the surface area. Much work has been done to determine the surface area of one of the components of multicomponent catalysts. Kolosov et al.¹³ examined the surfaces of platinum-supported catalysts (Pt–Al₂O₃, Pt–C, and Pt–SiO₂) for the conversion of hydrocarbons, using radial distribution functions and chemisorption methods. They found a strong metal-support interaction with the formation of a Pt/alumina phase with highly dispersed

and homogeneously distributed Pt atoms on the alumina surface. Emmett and Brunauer¹⁹ determined the surface area of iron on an ammonia-synthesized catalyst by means of carbon monoxide adsorption. The same technique was later applied to the determination of cobalt on kieselguhr and nickel on alumina oxide. However, these studies were all done for a catalyst that occupied a large surface area of the support. Borekov and Karnaukhov²⁰ later applied the same technique to determine the surface area for low concentrations of platinum catalysts, supported on silica gel, by using the surface adsorption of hydrogen.

Using the method of chemisorption to determine the surface area of a catalyst requires that the adsorbate forms a chemisorbed monolayer on the support surface. This requires a simple relationship to exist between the number of molecules adsorbed at the saturation point and the number of surface atoms present. This stringent requirement has precluded chemisorption from becoming a general method of surface determination. Nonetheless, surface adsorption is a very useful analytical technique when the metal is dispersed in a range that cannot be detected by physical measurements. Catalysts containing less than 1% platinum are very finely dispersed and will not be detected by physical measurements because the

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crystal size is smaller than 50 Å. The new approach of field emission scanning electron microscopy could be a very useful method for the analysis of catalyst systems.

Two types of catalysts are often mentioned: impregnated catalysts and cogelled catalysts. The former type is prepared by the calcination of high-purity alumina at approximately 590°C and the impregnation of the pellets with chloroplatinic acid, at room temperature, in sufficient volumes to fill pellet pores. By varying the concentration of the chloroplatinic acid solution, one can control the platinum content of the catalyst. The impregnated pellets are then dried overnight at 120°C, calcined at temperatures ranging from 205 to 593°C for 4 h, and then kept at 593°C for another hour. However, a cogelled catalyst is prepared by the simultaneous mixing of an alumina sol (5% solids as Al₂O₃) and chloroplatinic acid with aqueous ammonia. The gel is dried for approximately 12 h at 120°C, calcined at 260°C, ground and blended with a lubricant, formed into pellets, and calcined at 593°C.¹ The selection of the absorbate, the absorption parameters, and the influence of the support on hydrogen adsorption are important parameters in the chemisorption technique. Although the absorption of hydrogen occurs in some metals such as palladium, in platinum the amount of the absorbing hydrogen at temperatures greater than 400°C is negligible.⁴ The optimum adsorption temperature is the temperature at which the difference in the adsorptions of the adsorbent on the metal and on the support is maximum. This maximum is obtainable from the adsorption isobars. Because adsorption values on the alumina support differ widely, these values must be obtained for each new alumina in use. The chemisorption method for the determination of the surface area of alumina-supported platinum is accurate only when the following conditions are satisfied:² (1) hydrogen taken up by the platinum is adsorbed only on the surface and not in the interior; (2) hydrogen adsorption at 250°C and 24 cmHg corresponds closely to saturation with one hydrogen atom per platinum atom; and (3) when platinum is dispersed on the support, the support adsorbs the same quantity of hydrogen that it would have if the platinum had not been present.

Different views have been given concerning the manner in which hydrogen chemisorbs onto platinum. According to Adler and Keavney,¹ two hydrogen atoms adsorb for each platinum available. This was inferred from the observation that more hydrogen was adsorbed than there were platinum atoms available. From later work by Gruber,⁴ it became clear that one hydrogen atom is adsorbed for every platinum atom present. The latter observation is based on the assumption that the adsorption properties of the support toward hydrogen are not affected by the presence of up to 1% platinum on the surface but do affect the

TABLE I
Material Formulation and Polymerization Conditions for the Production of Hollow-fiber Carbon Membranes

Reagent	Amount (g)	Temperature (°C)	Stirrer speed (rpm)
DMF	270.00	—	—
AN	180.00	—	—
MA	2.46	—	—
AIBN	1.35	—	—
Polymerization temperature	—	55	—
Stirrer speed	—	—	2.5

degree of dispersion. The effects of the support can vary significantly, depending on the specific catalyst and the reaction under investigation.

To determine the specific area of the platinum from hydrogen adsorption values, we must assume that the crystallographic planes (100 and 110) of platinum are, on average, equally exposed on the surface.² Platinum specific areas, calculated on the basis of this assumption, correspond well with those obtained by Beeck.²¹ In the event of platinum being highly dispersed on the support surface, a hydrogen atom in the same vicinity could either adsorb onto the surface and remain near the previously adsorbed hydrogen atom or diffuse along the support surface until it encountered another vacant platinum atom. Although fine dispersions of platinum metal catalysts have been studied for a very long time, no reliable conclusions can be made yet concerning the nature of the supported catalysts when present in a chemical reaction. However, the surface area of the supported metal can be determined very accurately by means of the surface chemisorption of different gases. Hydrogen is most suitable for this purpose.

This article describes the results of an investigation into the effects of different platinum coating techniques on the microstructure and properties of hollow-fiber carbon membranes, with the purpose of relating them to the chemisorption of hydrogen onto the coated fiber carbon membranes.

EXPERIMENTAL

The production of hollow-fiber carbon membranes, the coating of the manufactured membranes through different techniques [i.e., solution coating, high-vacuum evaporation (HVE), and magnetron sputter coating], and the study of the coated membrane microstructures were carried out. A 2-cm piece of wire was used in each coating procedure. Table I shows the material formulations and polymerization conditions for the production of the hollow-fiber carbon membranes.

Synthesis of the hollow-fiber carbon membranes

Acrylonitrile (AN) was polymerized by the suspension polymerization technique, in which the monomer was subdivided (to allow effective cooling), yielding small and easily washable beads. The nitrogen inlet, condenser, and overhead stirrer were connected to three of the outlets. The fourth outlet was used to introduce the reactants to the reactor. *N,N*-Dimethylformamide (DMF; 270 g), 180 g of AN (containing the monomethyl ether of hydroquinone as a stabilizer to prevent the monomer from polymerizing spontaneously at room temperature), and 2.46 g of methyl acrylate (MA) were placed in the reactor together with 270 mL of distilled water. The stabilizer in the AN first had to be removed before the monomer could be used in the polymerization reaction. The monomer was washed with several equal volumes of dilute NaOH at 0°C. However, at this temperature, 7.2 wt % AN dissolves in the aqueous phase, whereas 2.1 wt % water dissolved in AN. Therefore, the required amount of AN had to be calculated carefully, with the amount lost in the washing process taken into account. The washed AN was dried overnight over calcium chloride pellets and filtered before being introduced to the polymerization mixture. The system was allowed to stabilize at 55°C before 1.35 g of the initiator, azobisisobutyronitrile (AIBN), was added. After 20 min, polymer particles began to precipitate, causing the solution to become milky. As soon as precipitation started, an additional 500–600 mL of distilled water was added to the polymerization mixture. The system was then stirred and left overnight so that a complete reaction was ensured. After cooling to room temperature, the copolymer was removed from the reactor and thoroughly washed with acetone (analytical-reagent grade; Saarchem Holpro, South Africa). After filtration, all the unreacted monomers, DMF, and water were removed. The remaining DMF and water were removed after a period of drying at 60°C in a vacuum oven.

Preparation of a spinning solution of the polyacrylonitrile (PAN)-based precursor

The PAN-based copolymer (36 g) and 4 g of poly(vinyl pyrrolidone) were added to 360 g of dimethyl sulfoxide (DMSO). The mixture was vigorously shaken until a uniform suspension was formed. The mixture was subsequently stirred overnight or until all the solids had dissolved. The homogeneity of the solution was best obtained by gentle agitation for a few hours on rollers. Although the solution was relatively clear, gel particles had to be removed before it was used for spinning. A warm solution (at 55°C) was filtered through a stainless steel filter (5- μ m sieve size) at 3 bar of nitrogen pressure. Air bubbles and dissolved gas in

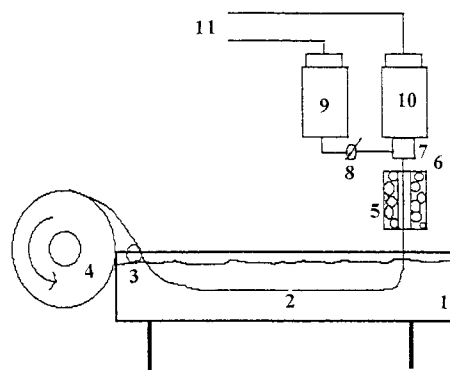


Figure 1 Spinning apparatus used to make the hollow-fiber carbon membranes: (1) coagulation bath, (2) spinning membrane, (3) small support roller, (4) rotating drum, (5) holder drum, (6) air gap, (7) stainless steel spinneret, (8) valve, (9) bore fluid, (10) spinning solution, and (11) nitrogen pressure.

the filtered solution were removed by the degassing of the solution overnight in vacuo.

Spinning of the hollow-fiber precursors

The precursors were spun into a water bath, at room temperature, and precipitated by the wet phase-inversion technique. The spinning equipment is shown in Figure 1. Stainless steel spinnerets of two different sizes were used. The spinning solution was pumped at moderate pressure through the spinneret and transversed in a threadlike manner through air before it precipitated in the water. The bore fluid, containing various mixture compositions of water and DMSO, was introduced into the bore of the spinneret at low pressures. Mass transfer took place between the DMSO in the spinning solution and in the bore solution with the water on the outside of the membrane. The pore structure was formed. After spinning, the precursors were leached in water at room temperature for 24 h and then in water at 55°C for approximately 48 h. During the leaching procedure, all the DMSO still present in the polymer matrix and bore was leached into the water, and the final precursor pore structure was stabilized again by a process of mass transfer. After leaching, the precursors were dried in air for approximately 2 days before they were ready to be carbonized.

Stabilization and carbonization of the PAN-based precursors

During the drying period, the membranes tended to adhere to one another. Therefore, they had to be carefully separated and inspected. Any precursors or parts of the precursors that had visible defects were removed. A silica powder (Aerosil 200) was subsequently used during the stabilization and carboniza-

tion processes to keep the precursors from sticking to one another.

The precursors were stabilized and carbonized in a single operation, inside a ceramic tube oven, under a nitrogen atmosphere. It was imperative for a nitrogen flow to be maintained so that all the byproducts would be removed. Furthermore, no air could be present during the stabilization and carbonization process because it would result in oxidation of the carbon structure. The precursors were first stabilized via heating at a rate of approximately $2^{\circ}\text{C min}^{-1}$ up to 350°C , and this was followed by carbonization via heating at the same rate up to 750°C . After carbonization, the membranes were washed first with water and then with acetone and were dried in air.

After drying, the hollow-fiber carbon membranes were ready to be coated with a platinum catalyst. The platinum metal was deposited onto the outer surface of the hollow-fiber carbon membranes by three different techniques: solution coating with chloroplatinic acid (the commonest method), vapor deposition (involving sublimation of the platinum metal), and magnetron sputter coating (the most effective technique).

Solution coating of the PAN-based precursors

A chloroplatinic acid solution was prepared from pure platinum metal and aqua regia. Platinum metal (Johnson Matthey Chemicals, London, England) was dissolved in boiling aqua regia, which was made up of one part nitric acid and three parts hydrochloric acid. Upon the dissolution of the platinum, an excess of hydrochloric acid was added to the solution to prevent the nitrate groups from complexing with the platinum. Upon crystallization, red-brown crystals of chloroplatinic acid, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, were formed. The crystals were dissolved in hydrochloric acid to form a solution of $8.1099 \times 10^{-2}\text{M}$ platinum. The hollow-fiber carbon membranes were soaked in the solution and then calcined at 150°C for 3 h. The platinum metal

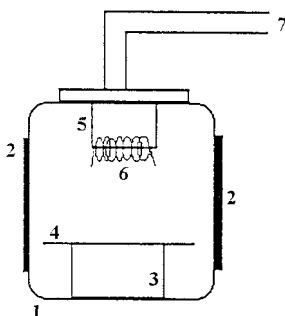


Figure 2 Apparatus used for the coating of platinum onto carbon membranes by means of HVE: (1) vacuum chamber, (2) doors to chamber, (3) holder, (4) stretcher with membranes, (5) element, (6) platinum wire, and (7) path to vacuum pump.

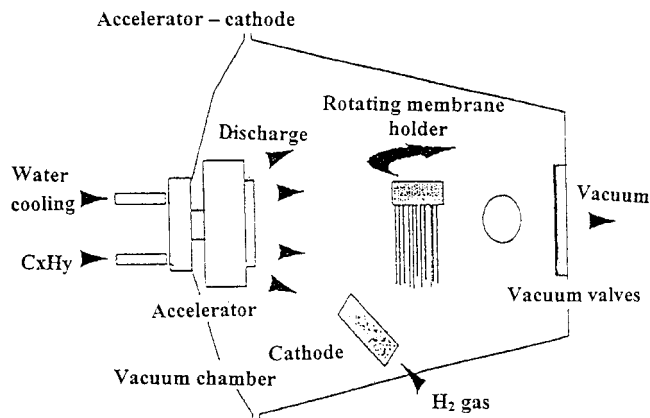


Figure 3 Apparatus used for the magnetron sputtering of carbon membranes.

was activated as a catalyst by reduction in a hydrogen stream at 150°C for 16 h.

HVE of platinum onto the hollow fibers

HVE involved the evaporation of a piece of platinum metal under high vacuum and the subsequent deposition of the metal onto a support surface. In this case, the support medium was the hollow-fiber carbon membranes. A 2-cm piece of platinum wire was attached to an element inside a high-vacuum chamber. The chamber was evacuated to a pressure of 10^{-5} Torr, and the element was turned on. The carbon membranes were at a much lower temperature than the element inside the vacuum chamber. Upon the evaporation of the platinum from the element, the platinum metal condensed onto the carbon surface. The platinum was deposited in an atomic form so that it would be very finely dispersed. The experimental setup used is shown in Figure 2.

Magnetron sputter coating

Hollow-fiber carbon membranes were coated with a layer of platinum, several micrometers thick, by magnetron sputter coating. A $100\text{-}\mu\text{m}$ -thick platinum foil was used as the magnetron target. Thirty hollow-fiber carbon membranes were positioned inside the specially designed circular Teflon holder, which was rotated at a speed of 30 rpm to ensure an even coating on the membrane surface. The pressure inside the vacuum chamber was kept constant at 10^{-5} Torr. The coating operation was carried out over a period of 2.5 min. The apparatus used for magnetron sputtering, with additional ionization, in which the hollow-fiber carbon membranes were coated with platinum, is shown schematically in Figure 3.

Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDAX) of the hollow fibers

A JOEL JSM-35 scanning electron microscope (model S-405), fitted with an EDAX analyzing facility, was used to study the morphology of and to detect metals in the hollow fibers treated with chloroplatinic acid solution. The analysis of metals, down to a metal concentration of approximately 1% by mass, is possible under a scanning electron microscope fitted with an EDAX analyzing facility.²² The scanning electron microscope was operated in the secondary imaging mode with an accelerating voltage of 25 kV, a working distance of 10 mm, and an aperture of 50 μm .

RESULTS AND DISCUSSION

Morphologies of the membranes prepared from small and large amounts of DMSO in the bore fluid

Figure 4 shows an SEM micrograph of a carbon membrane produced from a precursor that was spun with a bore fluid containing 25% DMSO and 75% water. The double-layer skin present was typical for precursors spun with a bore fluid containing large amounts of water. Figure 5 shows the SEM micrograph of a hollow-fiber carbon membrane produced from a precursor spun with a low amount of water in the bore fluid. The composition of the bore fluid had a considerable influence on the pore structure formed during the spinning procedure by mass transfer through the

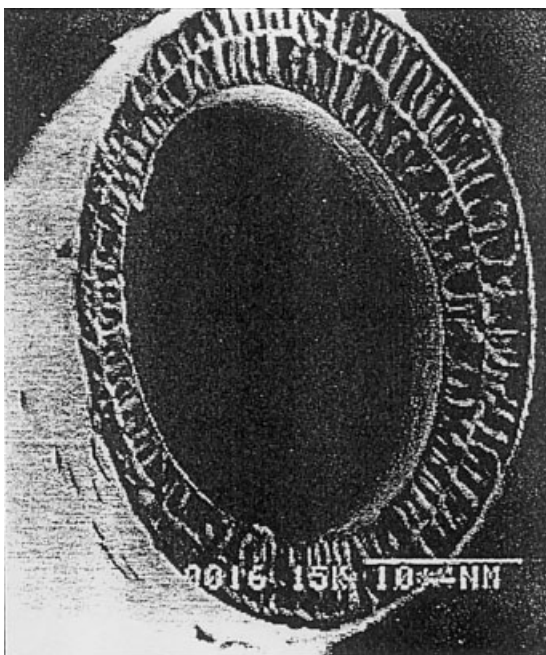


Figure 4 SEM micrograph of a hollow-fiber carbon membrane produced from a PAN precursor and spun with a low percentage of DMSO (25%) in the bore fluid.

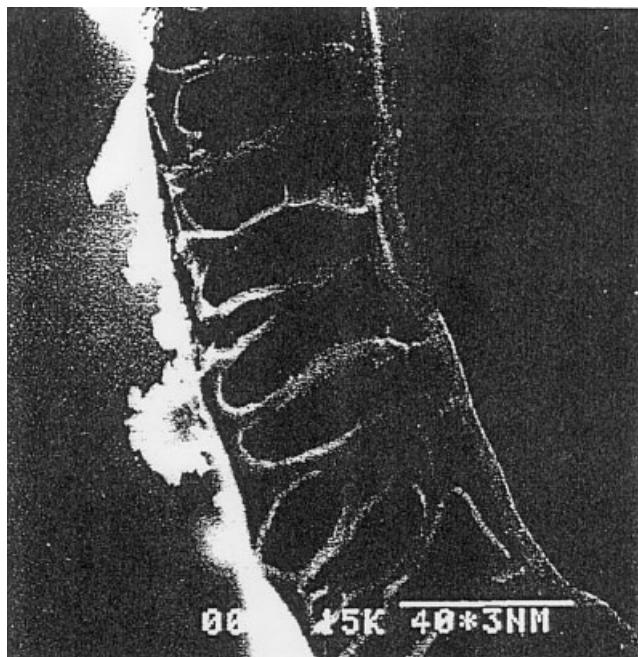


Figure 5 Magnified SEM micrograph of a hollow-fiber carbon membrane produced from a PAN precursor spun with a high percentage of DMSO in the bore fluid.

membrane. The driving force behind the mass-transfer process was the DMSO gradient, which had the highest value in the nascent polymer and the lowest value in the coagulation bath. A change in the DMSO concentration in the bore fluid, therefore, had a marked effect on the inner membrane surfaces. The membranes were spun with a skin on the outside and with a porous structure on the inside of the skin. High magnification with SEM showed no visible pores on the surface of the outside skin. However, the inside showed elongated pores. The area between the inner and outer skins contained fingerlike pores of various sizes. The largest pores were generally found near the inside skin, whereas the smallest pores were next to the outer skin. This membrane was considered suitable for reactor experiments because it provided a good surface onto which a catalyst layer could be deposited. Simultaneously, the pore structure provided a tortuous path for the reagents during the chemical reaction, so there was maximum contact between the reagents and the membrane itself.

Morphologies of the membranes not treated and treated with chloroplatinic acid

The hollow-fiber carbon membranes coated with a chloroplatinic acid solution were also studied with SEM and EDAX. The percentage of platinum on the surface of the membrane was too low to be detected by EDAX. Figure 6 shows an SEM image of the surface of the solution-coated membrane, whereas Figure 7

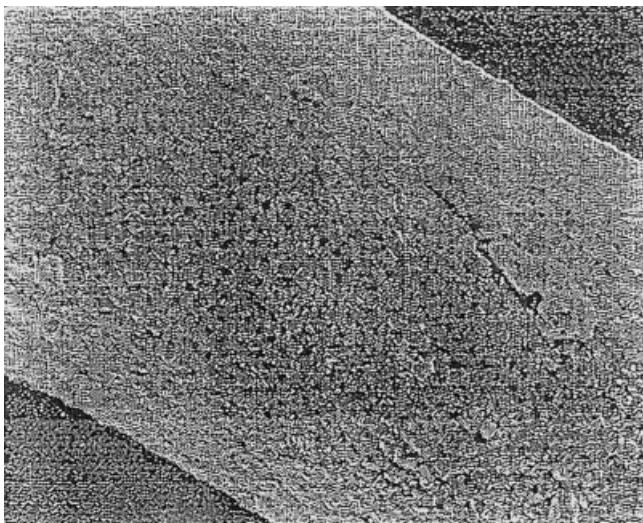


Figure 6 SEM micrograph of the outer surface of a carbon membrane coated with a chloroplatinic acid solution (500 \times magnification).

shows the surface of an uncoated membrane. A comparison of the two micrographs clearly shows that some coating was present on the coated membrane (Fig. 6). From Figure 6, it can be seen that the coating had grown on the surface in the form of small crystals. The membranes were incorporated into a reactor, and cyclohexane was dehydrogenated over the supposedly platinum catalyst on the surface of the membrane.²³ A conversion of 2% benzene was obtained. Moreover, there was not an even coating of platinum on the surface, and the fact that platinum could not be detected during an EDAX scan of the surface indicated that some of these crystals were not platinum but were most likely some platinum salt. To test this hypothesis, we subjected some coated membranes to calcination



Figure 7 SEM micrograph of the surface of an uncoated carbon membrane (800 \times magnification).

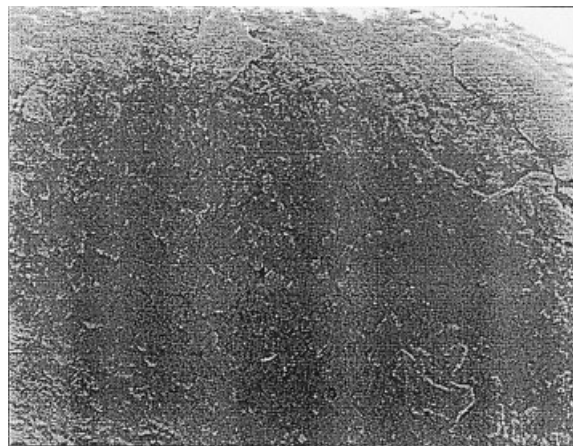


Figure 8 SEM micrograph of a carbon membrane coated with platinum by means of a high-vacuum technique (500 \times magnification).

for 1 h at 150 $^{\circ}$ C and then activated them overnight in a hydrogen atmosphere at 150 $^{\circ}$ C. These treated membranes were then placed in a reactor, and the dehydrogenation of cyclohexane was again carried out over the platinum coating.²³ This yielded a conversion of 4% benzene. It was concluded, therefore, that the crystals seen in Figure 6 were indeed a platinum salt of some sort and that this salt was reduced to platinum metal during the calcination process and the platinum metal was subsequently activated by the hydrogen treatment. This resulted in the higher conversion obtained.

Morphologies of the membranes coated with platinum by the HVE technique

The hollow-fiber carbon membranes subjected to HVE coating with platinum were studied with SEM and EDAX. Again, EDAX did not reveal any platinum on the surface of the carbon membranes. Because no other species were present in the vacuum chamber, the conclusion was that the percentage of platinum on the carbon surface was simply too low to be measured by EDAX. Figure 8 shows an SEM micrograph of a hollow-fiber carbon membrane that was platinum-coated by means of the HVE technique. From a comparison of this image with that of the uncoated carbon membrane in Figure 7, it is clear that a platinum coating was present on the outside surface of the membrane. No penetration of the carbon membrane pore structure was observed. As was the case for the solution-coated membranes, the coating could be explained by the manner in which the coating was conducted. The membranes were positioned on stretcher-like supports. The supports were then placed on a stand inside the vacuum chamber. Because the membranes were tubular, the coating operation had to be done twice to effect coatings on both sides. We

achieved this by turning over the stretcher with the membranes between the two coatings. The geometry of the membranes was such that some areas of the membranes were exposed to the element, from which the platinum was evaporated, in both instances, during both coating operations. This resulted in some areas of the membranes being coated twice, whereas other areas were not coated at all. The discontinuities in the platinum coating could have been the result of a large enough piece of platinum not being used during the coating operation. Rotating the membranes during the coating operation could have prevented the unevenness of the coating. Unfortunately, the coating apparatus could not be modified to incorporate this feature. The coated membranes were incorporated into a reactor and used for the dehydrogenation of cyclohexane over the platinum catalyst.²³ A conversion of 4% was obtained. In an effort to optimize the conversion, we activated the platinum catalyst overnight in a hydrogen atmosphere at 150°C. The membranes treated in this manner were again incorporated into reactors, and the dehydrogenation reaction yielded a 7% conversion.

Morphologies of the membranes coated by the magnetron sputtering technique

Hollow-fiber carbon membranes coated with platinum by means of magnetron sputter coating were studied with SEM. Varying the coating time varied the

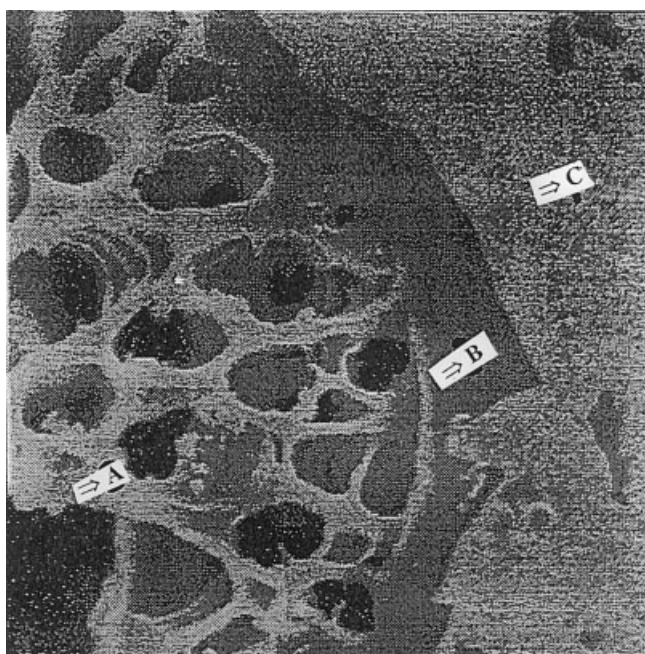


Figure 9 SEM micrograph of a carbon membrane coated with platinum by means of the magnetron sputter-coating technique: (A) the coated platinum layer, (B) the outer surface of the carbon membrane, and (C) the surface of the porous structure (800× magnification).

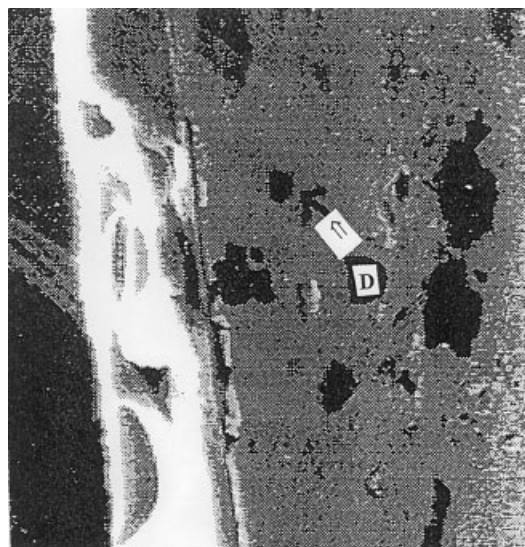


Figure 10 SEM micrograph of small openings (labeled D) present in the platinum layer on the carbon surface (800× magnification).

thickness of the coated platinum layer. The principles of the magnetron sputter coating were very similar to those of HVE, except that the platinum was bombarded with a magnetron beam or plasma. The platinum condensed onto the surface because the membranes surface was manipulated to be negatively charged. Figure 9 shows the SEM micrograph of a carbon membrane coated with platinum by the magnetron sputtering technique. The coated platinum layer (A), the outer surface of the carbon membrane (B), and the porous structure underneath (C) are clearly visible. Figure 10 shows the small openings (D) in the platinum layer. These openings were formed during the coating operation by the presence of dust particles on the membranes. The dust particles were coated with platinum during the coating operation, and when the membranes were removed afterward, the dust particles crumbled and left the openings in which they were previously positioned. Figure 11 shows the SEM micrograph of the length of a hollow-fiber carbon membrane. It shows the difference in the coated and uncoated surfaces of the carbon membrane. The darker area is the uncoated surface, and the brighter area is the platinum-coated area.

CONCLUSIONS

The composition of the bore fluid used during spinning has a considerable influence on the membrane pore structure that is formed during the spinning procedure. Platinum can be coated onto hollow-fiber carbon membranes from a chloroplatinic acid solution. The concentration of platinum in the solution determines the amount of platinum on the carbon membrane surface. Platinum deposits on the surface

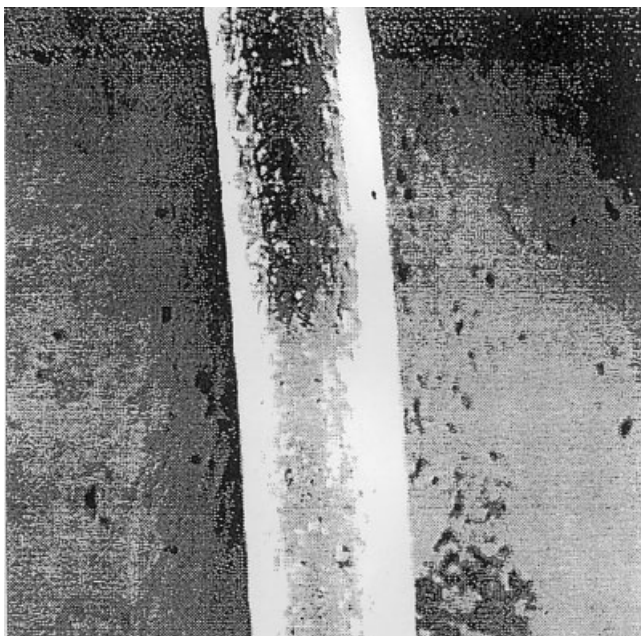


Figure 11 SEM micrograph of a hollow-fiber carbon membrane with one part coated with platinum (magnetron sputtering) and the other part (hidden by the sample holder) not coated.

of a hollow-fiber carbon membrane in the form of a platinum salt have to be reduced to platinum metal in a hydrogen atmosphere at a high temperature. Platinum coated onto the carbon surface by magnetron sputter coating forms an even, almost continuous layer on the surface. The discontinuities are the result of dust particles present on the membrane surface during coating.

Membranes treated with a chloroplatinic acid solution showed the growth of small crystals of platinum salts (which were reduced to platinum metal during the calcination process) on the surfaces of the membranes. There was an uneven coating of platinum on the surfaces of the membranes. Membranes subjected

to HVE showed discontinuities in the platinum coating.

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