

# Membrane Catalysis and the Platinum Group Metals

## A REVIEW OF TWO RECENT PUBLICATIONS

In response to the growing interest in membrane catalysis, Elsevier Science Publishers have recently produced two special issues on this topic. Papers on aspects of the preparation and use of membranes in catalytic reactors appeared in *Applied Catalysis A*, 1993, **96**, (1), and its sister publication, *Journal of Membrane Science*, 1993, **77**, (2+3). Each journal carried the abstracts of the articles appearing in the companion issue. A selective review of papers involving the platinum group metals is reported here.

### Membrane Gas Separation Technology

Membranes are an important part of many of today's chemical processes. In recent years hollow fibre, polymer membranes have achieved widespread acceptance for hydrogen recovery in the refinery and in ammonia manufacturing for nitrogen production from air, and the dehumidification and dehydration of air and natural gas. Membranes can be made from polymers, carbon, ceramics or metals. These membranes generally achieve their permselective properties by size exclusion based on their intrinsic microporosity. In contrast, noble metal membranes based on palladium and its alloys are selective for hydrogen permeation due to the hydrogen occluding ability of these materials. Membranes can offer significant advantages over other separation technologies including: improved selectivity, recovery, efficiency and environmental benefits.

### Combining Membrane and Catalyst Technology in Membrane Reactors

The selective removal of individual chemical reaction products via permselective membranes offers an opportunity to increase the conversion available in equilibrium limited processes. In addition the removal of a reaction product through a membrane can improve the selectivity of the process by the suppression of side

reactions which are dependent on the product concentration. Combining the permselective property of membranes with selected catalysts offers the prospect of improved yields through high single pass conversions, improved selectivity and hence improved process economics.

The use of the platinum group metals in this technology is assured due to their catalytic nature and the exceptional hydrogen permeability properties of palladium. In general platinum group metal-containing membrane reactors are found in one of two configurations, depending upon the method of combining the membrane and catalyst:

- (a) A disperse platinum group metal catalyst is incorporated into the surface of a microporous membrane to form a true catalytic membrane. In this configuration the membrane acts as the catalyst support. The membrane, often a porous ceramic, will display Knudsen selectivity based on its porosity characteristics.
- (b) A continuous palladium or palladium alloy film acts as a hydrogen permeable membrane. The palladium or palladium alloy film may also contribute its own catalytic properties to form a catalytic membrane. Alternatively, a hybrid reactor configuration may be preferred in which the membrane is placed in a reactor comprising a conventional fixed bed catalyst.

### Membranes Impregnated with Platinum Group Metals

A crucial aspect in controlling the catalytic properties of membranes containing disperse platinum group metals is the morphology and physicochemical properties of the catalyst phase, within the porous framework of the substrate material. It is desirable to achieve a high catalyst surface area without detrimental impact on the membrane permselectivity.

A paper in *Applied Catalysis* from D. Uzio, J. Peureux, A. Giroir-Fendler, J. Ramsay and

J.-A. Dalmon from the Institut de Recherches sur la Catalyse, France, and M. Torres from the Laboratoire d'Automatique et de Génie des Procédés, France, reported the preparation and characterisation of catalytic platinum deposited in a porous  $\gamma$ -alumina membrane. The  $\gamma$ -alumina membrane was a tubular ceramic membrane comprising three concentric layers with average pore diameters 12  $\mu\text{m}$  (outer), 0.2  $\mu\text{m}$  and 4 nm (inner). The preparation process resulted in platinum particles of average diameter 1.3 nm, with 0.2 weight per cent platinum being deposited in the inner layer. The deposited platinum appeared to have little effect on the pore size distribution of the impregnated, compared to the "bare", membrane. This effect was confirmed by the closely similar nitrogen permeabilities of the impregnated and "bare" membranes. Some larger particles up to 8 nm were also observed, but tended to be located at the surface of the membrane rather than within the porous structure.

Tests on the catalytic properties of the membrane for the hydrogenation of toluene, carried out under conditions designed to remove the effect of the membrane, showed that the properties of platinum particles within the porous framework were very similar to those of a conventionally supported catalyst (platinum 0.6 weight per cent, 1.5 nm average particle diameter). This group concluded that in future this type of membrane may find application in three-phase reactions as a method of improving the gas-liquid-solid interface.

A second publication in *Applied Catalysis* by N. K. Raman, T. L. Ward, C. J. Brinker, R. Sehgal, D. M. Smith, Z. Duan, M. Hampden-Smith of the University of New Mexico, U.S.A., and J. K. Bailey and T. J. Headley of Sandia National Laboratories, U.S.A., examined two procedures for the deposition of dispersed rhodium particles onto the ultramicroporous silica separation layer of a composite inorganic membrane. The first, involving wet impregnation of a silica membrane layer supported on a commercial microporous alumina support by  $\text{Rh}(\text{acac})_3$  solution, produced rhodium particles of about 4 nm within the composite structure. The second procedure used a silylating agent to react with

the surface silanol groups of the composite membrane, followed by reaction of the modified membrane with metal organic  $[(1,5\text{-COD})\text{RhCl}]_2$ . The metal particulates were produced by subsequent reduction of the composite membrane in hydrogen.

The composite membranes prepared by wet impregnation had reduced permeability to helium and nitrogen, compared to "bare" membranes. This was thought to be due to the penetration of rhodium into the porous structure and consequent pore blockage. The reduction step also produced cracks and damage in the silica layer as volatiles were lost and the rhodium crystallites were formed.

The silylation method also produced a composite membrane with reduced permeability to helium and nitrogen and showed a 60 per cent higher rhodium loading per unit mass of silica compared to the wet impregnated membrane. The rhodium crystallites were restricted to the surface of the silica layer with little penetration into the membrane. It was postulated that the size of the rhodium ligands (10 Å) was too great to allow penetration into the tortuous, ultramicroporous, silylated silica layer.

A publication in the *Journal of Membrane Science* by A. Julbe, C. Guizard, A. Larbot, L. Cot from the Ecole Nationale Supérieure de Chimie de Montpellier, France, and A. Giroir-Fendler from the Institut de Recherches sur la Catalyse, France, focused mainly on the preparation of microporous ceramic materials by sol-gel techniques. They showed it possible to prepare candidate structures suitable for use in membrane reactor systems and briefly described the insertion of metallic salts (specifically palladium chloride) to produce active, catalytic membranes. The reduction of palladium chloride in hydrogen produced homogeneously dispersed palladium nano-particles within a silica membrane matrix.

### **Palladium Alloy Membranes**

The size exclusion mechanism by which ceramic, carbon and some polymer membranes operate fundamentally limits the selectivity and throughput available with these types of

membranes. The use of dense metal foils, or thin supported films of palladium or palladium alloys provide an alternative technology capable of very high selectivity and throughput in hydrogen producing or consuming reactions.

A paper by T. S. Farris and J. N. Armor of Air Products & Chemicals Inc., Allentown, U.S.A., in *Applied Catalysis* examined the possible use of palladium-ruthenium membranes in liquid and vapour phase hydrogenation of alkenes, including cyclohexene, cyclo-octadiene and octadecene.

Conversions of only 2 to 5 per cent were achieved using a spiral palladium-ruthenium membrane tube (69 cm long, 0.1 cm diameter, surface area 0.0022 m<sup>2</sup>) in liquid phase reactions. However similar reactions in the vapour phase, conducted previously, using 5 cm diameter foil disks of palladium and palladium alloys, gave far higher conversions. Conversions of up to 35 per cent were achieved for the hydrogenation of cyclohexene at 423 K over 100 μm thick palladium-6 per cent ruthenium foils. It was concluded that the low conversions available with palladium-ruthenium foil membranes indicated limited practical applicability of this type of membrane for liquid phase hydrogenation of alkenes.

The use of a membrane reactor comprising a composite palladium membrane with fixed bed catalysts based on platinum group metals and base metals was reported in a paper by T. Matsuda, I. Koike, N. Kubo and E. Kikuchi of Waseda University, Japan, in *Applied Catalysis*. This group attempted the low temperature dehydrogenation of organic molecules and in particular the dehydrogenation of isobutane to isobutene. Using a membrane in such a reaction should result in improved yields at any given temperature, and should enable the reaction to run at temperatures below current commercial processes (around 900 K).

Initial experiments were carried out without the membrane in the reactor to test the equilibrium conversion available with the catalyst only system. A variety of platinum group metals and base metal catalysts were screened for activity as low temperature dehydrogenation catalysts for isobutane. A platinum on alumina catalyst was found to be the most active, with almost twice

the activity of a Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst tested under the same conditions. The conventional catalyst system gave a product stream containing methane, ethane, propane and other C<sub>4</sub> compounds, with isobutene selectively formed only at very low conversion levels.

The palladium composite membrane was prepared by electroless deposition of a thin layer of palladium onto a porous alumina cylinder of average pore diameter 200 nm. The membrane composite was placed in the reactor and the dehydrogenation experiments were re-run; the situation changed dramatically with the platinum/alumina catalyst exhibiting lower activity than the Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>. Isobutene yields were far higher than those obtained in the catalyst-only system and an analysis of the product distribution showed that isobutene was selectively formed, irrespective of the reaction temperature. It was postulated that the selective removal of hydrogen via the palladium membrane was effective in suppressing the undesirable side reactions (hydrogenolysis and hydroisomerisation) which occurred in the conventional reactor system.

The lower activity of the platinum/alumina catalyst in the membrane reactor configuration appeared to be a function of catalyst deactivation due to coke formation within the reactor. Tin added to the platinum on alumina catalyst effectively reduced the tendency to coke and increased the isobutene yield with increasing activity, up to a tin content of 0.2 weight per cent. The overall reaction in the membrane reactor was controlled by the reaction rate and was not limited by the hydrogen flow through the membrane.

A paper in *Applied Catalysis* from V. M. Gryaznov, O. S. Serebryannikova and Yu. M. Serov from the Russian Peoples' Friendship University, Moscow, and M. M. Ermilova, A. N. Karavanov, A. P. Mischenko and N. V. Orekhova of the A. V. Topchiev Institute of Petrochemical Synthesis, Moscow, described the preparation of a variety of composite palladium-based membranes and their use in membrane reactor systems. Professor Gryaznov has for many years been a leading exponent of membrane catalysis, concentrating mainly on the effect of

Characteristics of Composite Palladium Membranes				
Substrate material	Palladium alloy membrane	Thickness, $\mu\text{m}$	Hydrogen flow, $\text{m}^3/\text{m}^2/\text{h}$	Pressure differential, MPa
Polyarylyde	Pd-6%Ru	0.4	13.8	1.0
Stainless steel	Pd-6%Ru	10	120	2.0
Stainless steel	Pd-6%In-0.5%Ru	1.5	4	0.1
MgO-Y <sub>2</sub> O <sub>3</sub>	Pd-6%Ru	10	108	1.0

palladium membranes as true catalytic membranes in various hydrogenation/dehydrogenation reactions.

The preparation of composite palladium alloy membranes consisting of a thin continuous metal layer supported on porous polymer, metal or ceramic, was discussed. The composite nature of these devices is intended to maximise the hydrogen permeability of the membranes while reducing the noble metal content.

The first type of membrane described, consisted of a polyarylyde material sputter coated with a thin film of either a palladium-6 per cent ruthenium or a palladium-4 per cent tin alloy. The polyarylyde substrate has an advantage over other polymers of being stable to temperatures above 623 K. Composites with a metal layer only 0.4  $\mu\text{m}$  thick were permeable only to hydrogen and resistant to thermal cycling between 313 and 473 K in hydrogen. These membranes, modified by cobalt sputtered onto their surface, were tested for activity in the vapour phase hydrogenation of 1,3-pentadiene where conversions of 99.8 per cent and selectivities towards pentenes of 92.7 per cent were achieved. These results were much better than could be achieved by conventional hydrogenation catalysts.

Another group of composite membranes were prepared on porous stainless steel substrates. However at elevated temperatures the palladium alloy films reacted with the substrate causing a drastic reduction in the hydrogen flux which the membrane could sustain. Sputtered thin tungsten, molybdenum or other refractory interlayers between the substrate and palladium film were

effective as diffusion barriers and stabilised the hydrogen flow.

Membranes based on a porous magnesia-15 per cent yttria substrate with average pore diameters around 0.3  $\mu\text{m}$  and a total porosity of 50 per cent were prepared by sputtering. The hydrogen permeabilities of these composites were stable during a 1000 hour test, with no defects apparent in the palladium alloy film or at the film-substrate interface.

Details of some of the composite membranes are shown in the Table illustrating that the hydrogen permeabilities of such thin composite membranes are up to 100 times those of conventional foil membranes while using only a fraction of the amount of noble metal.

This group also worked on foil membranes with the specific intention of modifying their surface catalytic properties. In one experiment cobalt was incorporated into the surface of palladium-10 per cent ruthenium foils. The modified foils were tested for activity in a carbon monoxide hydrogenation reaction along with untreated palladium-ruthenium and palladium-cobalt foils at 523 K. Seven per cent of C<sub>2</sub>-C<sub>3</sub> alkenes were produced on the modified foil. The removal of hydrogen through the modified foil increased the alkene concentration to 40 per cent. This result differs drastically from the results obtained with unmodified palladium-ruthenium and palladium-cobalt foils.

In another modification to a foil membrane a palladium-6 per cent indium-0.5 per cent ruthenium membrane was modified by embedding active alumina into the foil surface. The

resulting membrane was active for acetone condensation to 2-methylpentanone-4.

The technical and commercial interest in preparing thinner, more cost effective palladium alloy membranes was reflected in a publication in the *Journal of Membrane Science* by J. Shu, B. P. A. Grandjean, E. Ghali and S. Kaliaguine of Laval University, Canada. They reported a method for the preparation of palladium-silver thin films on a porous stainless steel substrate by the simultaneous electroless deposition of the two elements from a single bath containing palladium and silver salts. In order to ensure continuous plating the silver component was added to the plating bath after 5 minutes predeposition of palladium. The metal film thus produced required a thermal treatment in hydrogen to homogenise and fully crystallise the membrane.

A paper by J. P. Collins, J. D. Way and N. Kraisuwansarn of Oregon State University, U.S.A., in the *Journal of Membrane Science* employed a mathematical model to investigate catalytic ammonia decomposition in a membrane reactor. Advanced power generation systems, such as integrated gasification combined cycle processes using coal or other fossil fuels, produce a gas stream containing trace amounts of ammonia and other toxic and corrosive impurities, such as hydrogen sulphide. Due to the high temperatures of the associated reactions the removal of these impurities by conventional gas separation processes is impossible. Conventional fixed-bed catalytic reactors would also be of limited use, because the high concentrations of hydrogen and nitrogen in the gas stream would make the decomposition reaction equilibrium limited. A mathematical model analysis showed that ammonia conversions above equilibrium could be obtained by using ceramic membranes capable of Knudsen diffusion selectivity. To achieve high conversions membranes with a selectivity for hydrogen over nitrogen of greater than 50 would be required. Membranes based on a palladium alloy are particularly attractive for such operations due to improved conversions and process efficiency available with this highly selective membrane. However a serious problem for such membranes is degradation due to

hydrogen sulphide at elevated temperatures. A strategy for removing the sulphur and nitrogen contaminants in the gas stream of advanced coal-based power generation systems involved a molten salt liquid membrane to remove the hydrogen sulphide prior to the palladium membrane.

A method of using a palladium based membrane in the presence of hydrogen sulphide or other corrosive gases was reported in the *Journal of Membrane Science* by D. J. Edlund and W. A. Pledger of Bend Research Inc., U.S.A. Their work was based on a membrane system capable of facilitating the thermal decomposition of hydrogen sulphide, using a hydrogen permeable composite membrane. This consisted of a vanadium foil (30  $\mu\text{m}$  thick) chosen for its high hydrogen permeability and resistance to embrittlement, sandwiched between a palladium and platinum foil both 25  $\mu\text{m}$  thick. The palladium is present on the permeate side of the working membrane to protect the vanadium from oxidation during start-up and shut-down procedures. The platinum layer on the feed side of the working membrane, provides chemical resistance to the hydrogen sulphide and acts as a catalyst for hydrogen sulphide thermolysis. Thin layers of silica (1 to 10  $\mu\text{m}$ ) separated the noble metals from the base metal to avoid interdiffusion at the working temperature of the membrane (973 K).

The platinum-vanadium-palladium composite membrane was tested in a feed-stream of pure hydrogen sulphide and a 1.5 per cent hydrogen sulphide/nitrogen mixture alongside a palladium/vanadium composite with no platinum protective layer. While the platinum coated membrane did not degrade during exposure to hydrogen sulphide at 973 K, the palladium only membrane failed by catastrophic corrosion-induced rupture within a few seconds of exposure to the feed stream. The platinum-vanadium-palladium composite membrane was able to drive the decomposition of hydrogen sulphide to greater than 99.4 per cent of complete conversion. The hydrogen flow through the membrane was rate limiting at conversions above equilibrium, so a membrane with a higher hydrogen permeability would be more effective. The low hydrogen permeability of the platinum layer

determines the flow through the composite membrane and therefore in industrial usage the platinum layer thickness would be minimised. This study shows that a membrane reactor process could be economically and technologically feasible for the decomposition and separation of hydrogen sulphide in an environmentally friendly fashion. Applications proposed for this type of technology include the clean-up of coal-derived gases, recovery of hydrogen from hydrogen sulphide containing refinery gas streams and the sweetening of sour natural gas.

## Outlook

The papers collected in the special issues of *Applied Catalysis* and the *Journal of Membrane Science* illustrate a variety of approaches for har-

nessing the potential of combined membrane and catalyst technologies. These publications represent the latest in an increasing number of recent articles on this topic, a testament to the exciting potential of these techniques. The use of platinum group metals in membrane reactors is justified by their unique catalytic properties and the dividend available through the "process intensification" which they can produce. Industrial applications for membrane catalysis will depend on developing effective, commercial scale, membrane reactor systems in a more economical manner. This task will require a multi-disciplinary approach involving ceramicists, catalyst scientists, chemists and materials scientists. Judging by the reviewed papers, this process is already underway. M.L.D.

## The Use of Rhodium in Selenium Detection

There is a need to be able to measure small traces of selenium in ground water and river water quickly and accurately, because of the damage that a potential toxic level can cause to the environment. In the past selenium has been detected by electroanalytical techniques, such as anodic stripping procedures and more recently by cathodic stripping, which is based on the preconcentration and subsequent reduction of mercury and copper selenides.

Now, researchers at the New Mexico State University, Las Cruces, U.S.A., have discovered that the sensitivity of selenium detection by a cathodic stripping voltammetric procedure can be greatly improved by adding rhodium instead of copper selenide to the sample mixture (J. Wang and J. Lu, "Ultratrace Measurements of Selenium by Cathodic Stripping Voltammetry in the Presence of Rhodium", *Anal. Chim. Acta*, 1993, 274, (2), 219-224).

This extremely sensitive cathodic stripping voltammetric method is based on the accumulation and subsequent reduction of a rhodium selenide layer on the hanging mercury drop electrode. Insoluble layers of rhodium selenide are formed on the mercury surface during the preconcentration step. The reduction of the accumulated rhodium selenide gives a sharp cathodic stripping response which is around ten to fifty times larger than the analogous copper or mercury selenide peaks, respectively. The best assaying results have been obtained for a sample containing 0.1 M sulphuric acid solution, 10 µg/l rhodium and preconcentration at

- 0.2 V. A fast linear scan follows which gives a high signal to background characteristic and faster assay. Under optimum conditions, an extremely low detection limit of 0.5 ng/l of selenium can be achieved, following a three minute preconcentration.

This method is fast, ultrasensitive, giving high selectivity and precision, and can be applied for selenium measurements in complex environmental and biological samples.

## Platinum Alloy Film in Optics

To achieve useful total reflection optical systems for imaging and focusing soft X-rays, the mirrors used are required to have smooth surfaces and to increase the grazing angles of incidence. Materials of high bulk density coated on the mirrors can enlarge the grazing angle. Film surfaces can be made smoother by combining materials.

Researchers in Japan have now developed and characterised high density platinum-palladium alloys which give smoother film and better performance as reflecting surfaces (K. Nakajima, S. Sudo, H. Kanda, T. Ishii and S. Aoki, *Jpn. J. Appl. Phys.*, 1993, 32, (3A), 1275-1278).

Sputter deposited platinum-palladium alloy was characterised by X-ray reflectivity measurements. Grain growth of the polycrystalline platinum film was controlled by adding small amounts of palladium. A platinum-1.8 atomic per cent palladium film has a 1 ~ 6 per cent higher reflectivity than a pure platinum film at grazing angles up to about 1°.