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Membrane catalysis

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Abstract

The main events in the development of membrane catalysis are presented in this paper. The pioneering studies of Graham performed in London were continued by Zelinskii in Moscow and by Snelling in the USA. The finding by Frost in the USSR that hydrogen evolved from Pd film is much more active in hydrogentation than feeded as gas with the hydrogenable substance stimulated the researchers of several countries, including the author of this paper, who proposed the method for carrying out simultaneously dehydrogenation on one surface of membrane catalyst and hydrogenation by the diffused hydrogen on the other surface. Similar reactions couplings were carried out later but independently performed by Pfefferle in the USA. The types of hydrogen porous membrane catalysts for selective hydrogenation and dehydrogenation elaborated in Russia were described in next sections. The final section deals with the examples of coupling of hydrogen evolution and consumption reactions on membrane catalyst as well as on the systems of membrane and granular catalysts.

Keywords: Membrane catalysis; Palladium black; Hydrogenation; Hydrodemethylation

1. Introduction

In 1866 Graham initiated the area of palladium usage for hydrogen separation from gaseous mixtures and its catalytic activation for chlorine–water transformation into hydrochloric acid and other liquid phase reactions at room temperature. In 1898 Zelinskii at Moscow University, combined hydrogen evolution during hydrochloric acid reaction with zinc and hydrogenation by a palladium sponge covering the zinc granules. This was the first composite membrane catalyst. In 1915, Snelling in the USA patented hydrogen removal through Pt or Pd tubes from a reactor with a granular catalyst of dehydrogenation. Twenty years later Dobichin and Frost in the USSR discovered that there is an increase in catalytic activity of hydrogen evolved from a Pd film in comparison with gaseous hydrogen. Hydrogenation on Pd and other metallic membranes by hydrogen electrochemically produced on the opposite surface of this membrane was investigated in 1935 at Moscow University by Kobosev and Monblanova and more extensively in 1949 in the UK by Ubbelohde. Wagner and Hauffe in Germany in 1939, Wood and Wise in the USA in 1966 and later many other scientists studied the hydrogenation on palladium and palladium alloy membranes by hydrogen supplied as a gas to the other surface.

In 1964, a method was proposed [1] for carrying out simultaneously the evolution and consumption of hydrogen which comprises conducting these pro-

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cesses in a reactor divided by a partition made from a material that is selectively permeable to hydrogen only and serves as a catalyst. A palladium tube electrolytically coated with palladium black was used as membrane catalyst. Cyclohexane vapor was introduced into the tube, while the space between the tube wall and the reactor shell was filled with *o*-xylene vapor. At a temperature of 703 K, the yield of benzene as a result of cyclohexane dehydrogenation was equal to 43%. The hydrodemethylation of *o*-xylene yields 6% of benzene on the other side of the membrane catalyst. Quite independently Pfefferle [2] performed ethane dehydrogenation to ethylene to the extent of 0.7% over a palladium–25 wt.% silver tube, wherein the hydrogen evolved was oxidized on the other side of the membrane catalyst by oxygen diluted with nitrogen.

This paper presents some new data about membrane catalyst usage for selective hydrogenation, dehydrogenation and coupling of these reactions.

2. Selective hydrogenation

A hydrogen porous membrane catalyst provides independent control of the surface concentrations of hydrogen and of hydrogenatable substance. It suppresses their harmful competitive adsorption which is inevitable on conventional hydrogenation catalysts. Experiments with 100 micron thick foils of palladium binary alloy with 15% rhodium were performed at Topchiev Institute of Petrochemical Synthesis (TIPS). The foil was clamped between stainless steel end plates and separated the reactor into two chambers. Hydrogen was supplied to one of the chambers and the vapor of a hydrogenatable substance in an inert gas was introduced into another chamber. The reaction products were analyzed by GLC.

It was found that unlike the common catalyst, this membrane catalyst converted olefins into paraffins in the presence of aromatic hydrocarbons without the hydrogenation of the aromatics. This result is important for the upgrading of aromatic hydrocarbons because the selectivity of hydrogenation of the olefin admixture was 99.99%. The productivity of one square meter of the membrane catalyst per hour was 1.2 mol of olefins. An increase in the aromatic hydrocarbon content from 25% to 52% in the mixture with paraffins and 3% olefins did not change the completeness of olefin hydrogenation.

A palladium–9.8% ruthenium membrane catalyst proved to be selective for cyclopentadiene hydrogenation into cyclopentene – a synthetic rubber monomer. Cyclopentadiene is usually obtained by gasoline pyrolysis and includes admixtures of 1,3-pentadiene and isoprene. That is why the experiments were performed to elucidate the influence of these admixtures on cyclopentadiene hydrogenation. The conversion and selectivity towards cyclopentene did not diminish with increase in 1,3-pentadiene or isoprene content up to 20%.

A pilot-plant catalytic membrane reactor for liquid phase hydrogenation was constructed at TIPS and the A.A. Baikov Institute of Metallurgy, RAS, Moscow, Russia. Disks of mechanically strong and corrosion stable palladium–indium–ruthenium alloy foils 70 micron thick were used in a new construction of a catalytic membrane reactor which may be used for ultra-pure hydrogen production as well. Two specially corrugated disks are welded to a stainless steel ring. Such elements are combined in a series with gas distribution accessories. Hydrogen is fed inside the elements at pressure up to 10 atm and the outer surface is used as a catalyst for selective hydrogenation. Liquid reactant is distributed uniformly along the membrane catalyst surface. The pressure drop across the membrane catalyst may be up to 5 atm. Hydrogen-rich industrial gaseous mixtures may be used for hydrogenation instead of pure hydrogen. The reactor has been tested in dehydrolinalool hydrogenation into linalool of perfumeric quality and in the production of eatable hard fats from liquid plant oils. The target substances are free of the products of thermal destruction because of the participation of atomic hydrogen in the hydrogenation at lower temperature. Vitamins, dyes and other pure substances may be produced as well. The productivity of this reactor is 100 t per year.

A composite nickel membrane catalyst promoted with rare earth oxides for selective hydrogenation of acetylenic hydrocarbons has been prepared at TIPS. A composite membrane catalyst was also prepared by coverage of one side of the porous stainless steel sheet by a thin layer of titania and by the introduction of a nickel ultradispersed powder with 0.5 wt.% La_2O_3 or Ce_2O_3 powder. An electron microscopy study showed that the titania coverage decreased the average pore diameter of the stainless steel sheet from 1.9 to 0.14 micron. The membrane structure did not change after heating at 673 K for 15 h. The composite membrane catalyst was inserted into the steel reactor as a partition between two chambers. Hydrogen flows through one chamber and the hydrocarbon to be hydrogenated flows through the other chamber. The pressure drop between the two chambers may be up to 10 atm.

Dehydrolinalool hydrogenation into perfumeric quality linalool was performed on two membrane catalysts with different modificators. Ceria is twice as effective as La_2O_3 in giving the increase in productivity.

At the Russian University of People's Friendship (RUPF), a method for producing a porous support covered by a dense film of palladium alloy 1 or 2 micron thick has been developed. One support was prepared by electrochemical oxidation of an electropolished pure aluminum foil 100 micron thick in oxalic acid. The freshly prepared membrane was 135 micron thick and consisted of two phases, γ-alumina and boehmite. Cylindrical channels of 100 nm in diameter with regular distances 300 nm between each crossed the membrane. The important property of such a membrane is the metal aluminum frame along its contour which permits the hermetic sealing of the membrane into a diffusion cell or a catalytic membrane reactor.

Other composite membranes were prepared on porous stainless steel sheets or on compressed refractory oxide plates. Introduction of ultradispersed powders of catalytically active metals into the porous volume of the above support permits one to prepare a composite two-layer membrane catalyst. The upper layer is a fine film of palladium alloy which is a source of atomic hydrogen. It participates in hydrogenation reactions after spillover along the metal powder surface in the porous volume of the second layer.

At RUPF and Lomonosov Moscow State University, nitromethane (NM) reduction was performed by a palladium foil 100 micron thick which divided two parts of an electrochemical cell. The potentials of the different sides of this foil were controlled independently by two potentiostats. The membrane surfaces were covered electrochemically by palladium layers several microns thick. Their roughness factors changed from 50 to 130 for different membranes. For comparison, NM reduction was also studied on palladized platinum wire. The electroreduction rate by the membrane electrode was higher than that of the palladized wire, probably because of the optimization of the surface concentrations of hydrogen atoms and NM. Adsorption of silver atoms on the membrane or on the wire electrode increases the reduction rate but copper or cadmium adsorption depresses this reaction.

3. Dehydrogenation with removal of hydrogen through membrane catalysts

Dehydrogenation of cyclohexanol (CHL) to cyclohexanone (CHN) was carried out at atmospheric pressure in an all-metal, flow-type, two-loop installation. Each loop contained one of the two zones of the reactor, separated from each other by the membrane catalyst and a bubbler thermostat.

The main product of cyclohexanol dehydrogenation by palladium alloy membrane catalysts is cyclohexanone. At temperatures above 480 K, cyclohexene or phenol is formed, depending on the nature and concentration of the second component of the palladium-based alloy.

The rate of hydrogen removal from the cyclohexanol dehydrogenation zone of a catalytic membrane reactor is lower than the rate of hydrogen transfer through this membrane catalyst during passage of the hydrogen-inert gas mixture under the same conditions. The ratio of hydrogen concentrations in both chambers of the catalytic membrane reactor proved to be a function of the membrane catalyst content. For example, the hydrogen concentration in the products of cyclohexanol dehydrogenation by binary alloys palladium with 10% ruthenium or 5% rhodium was higher than that in the hydrogen elution chamber. The opposite situation was found during cyclohexanol dehydrogenation by Pd–Ru–Pb and Pd–In–Ru membrane catalysts when cyclohexene was formed as by-product. Unlike the above catalysts, Pd–Ru and Pd–Rh catalysts give phenol as a by-product of cyclohexanol dehydrogenation. The mentioned difference in hydrogen concentrations at both surfaces of the binary and ternary membrane catalysts may be caused by a diminution of the recombination rate of the hydrogen atoms and of desorption of di-hydrogen molecules in the dehydrogenation zone in the presence of cyclohexene in comparison with the rate of diffusion of hydrogen atoms through the ternary palladium alloys. Hydrogen desorbed in the dehydrogenation zone is slowly adsorbed on the surface covered by cyclohexene. That is the reason for the hydrogen permeability decrease.

The amount of hydrogen diffused from the dehydrogenation zone may be increased by its usage in hydrogenation or oxidation on the other surface of the membrane catalyst. However, the complete removal of hydrogen was not achieved even during hydrogen oxidation. This means that the limiting step of hydrogen transfer is hydrogen atoms recombination on the exit surface of the membrane catalyst.

4. Coupling of hydrogen evolution and consumption reactions on the monolithic membrane catalysts

Hydrogen transfer from the zone of its formation increases not only the equilibrium yields of this reaction but also its selectivity. For example, if, together with dehydrogenation, cracking of the initial hydrocarbon takes place, the removal of the hydrogen formed through a membrane catalyst facilitates dehydrogenation, but the cracking products remain in the same reaction space and retard the side reaction.

Table 1 summarizes the first applications of palladium and palladium alloys monolithic membrane catalysts for reaction coupling. The drawback of a monolithic membrane catalyst is the small catalytic surface area per unit volume of the reactor. The surface area may be increased by the formation of Raney type catalysts as a result of the introduction of chemically active metal into the surface layer of membrane catalyst and removing the introduced metal by acid. Another method of increasing the monolithic membrane catalyst surface is the formation of a columnar structured layer of the same content on the surface by magnetron sputtering. The next step is the increasing of the surfaces of both sides of the membrane catalyst by covering the porous refractory support by layers of catalysts. The system of a support with two layers of catalytically active materials permits the coupling of two reactions. The examples of monolithic membrane catalyst with a columnar structure on one surface are given in Ref. [3].

Systems involving monolithic membranes and granular catalysts have been investigated by many authors. Table 2 includes examples of such systems used for the coupling of hydrogen evolution and consumption reactions.

The increase in membrane catalyst surface per unit volume of the reactor shell was achieved by the use of thin-walled palladium alloy tubes in the form of plane double-start spirals. The spirals are stacked one on the

Table 1
Applications of palladium and palladium alloys monolithic membrane catalysts for reactions coupling

Reactions	Catalyst	*T* (K)	Authors
A: dehydrogenation of cyclohexane; B: demethylation of *o*-xylene	Pd, tube	703	Gryaznov (1964)
A: dehydrogenation of ethane; B: oxidation of hydrogen	Pd-25Ag, tube	625	Pfefferle (1965)
A: coupling of dehydrogenation of *trans*-butene-2; B: demethylation of toluene or hydrogenation of benzene	Pd, Pd-20Ag, tube	653–713	Gryaznov et al. (1966)
A: dehydrocyclization of undecane; B: hydrodemethylation of dimethylnaphtalene	Pd-5.9Ni, foil	860	Gryaznov et al. (1968)
A: dehydrogenation of isoamylenes; B: hydrodemethylation of toluene or oxidation of hydrogen	Pd-5.9Ni, foil	723	Gryaznov et al. (1975)
A: dehydrogenation of isopropyl alcohol; B: hydrogenation of cyclopentadiene	Pd-10Ru, foil	493	Mikhalenko et al. (1977)
A: borneol dehydrogenation; B: cyclopentadiene hydrogenation	Pd-5.9Ni; Pd-10Ru; Pd-15Rh, foils	473–543	Smirnov et al. (1981)
A: butane dehydrogenation; B: hydrogen oxidation	Pd-9.8Ru; Pd-5.5Sn; Pd-23Ag, foils	753–823	Orekhova and Machota (1981)
A: cyclohexanol dehydrogenation to cyclohexanon; B: cyclopentadiene hydrogenation to cyclopentene	Pd-9.8Ru, foil	500–550	Basov and Gryaznov (1985)

Table 2
Systems of metal-containing membrane and granular catalysts for reaction coupling

Reactions	Membrane	Catalyst	*T* (K)	Authors
A: borneol dehydrogenation to camphor; B: 1,3-pentadiene hydrogenation	Pd-5.9Ni, Pd-10Ru, Pd-10Rh, foils	Cu, wire; membrane catalyst	520	Gryaznov et al. (1977)
A: methane dimerization; B: hydrogen oxidation	Pd, tube	Pt-Sn/Al_2O_3; Rh/SiO_2; membrane catalyst	630–710	Andersen et al. (1989)
A: butane dehydrogenation to butadiene; B: hydrogen oxidation	Pd-9.8Ru, foil	Cr_2O_3–Al_2O_3; membrane catalyst	723–823	Machota and Orekhova (1981)
A: cyclohexane dehydrogenation to benzene; B: hydrogen oxidation	Pd, tube	Pt/Al_2O_3; membrane catalyst	470	Itoh (1990)
A: butene-1 dehydrogenation; B: hydrogen oxidation	Pd, foil	Cr_2O_3–Al_2O_3; membrane catalyst	720	Zhao and Govind (1990)
A: cyclohexane dehydrogenation to benzene; B: 1,3-pentadiene hydrogenation	Pd-6Ru, foil	Pt-Re/Al_2O_3; membrane catalyst	490	Orekhova et al. (1991)

other, the inlet and outlet ends of the tubes being secured in tubular headers positioned perpendicular to the plane of the spiral. This constructional arrangement enables the volume of the apparatus to be filled with tubes to a maximum. The blocks of spirals were mounted within the reactor shell and were joined in parallel to diminish hydraulic resistance to flow inside the tubes. Stainless steel reactor with 200 spirals with total length of tubes of 400 m have been used for hydrogenation of acetylenic alcohols into the corresponding ethylenic alcohols. In TIPS, a laboratory scale reactor of the same type has been tested for the selective hydrogenation of phenylacetylene into styrene.

References

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