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### METAL CONTAINING MEMBRANES FOR THE PRODUCTION OF ULTRAPURE HYDROGEN AND THE RECOVERY OF HYDROGEN ISOTOPES

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# **METAL CONTAINING MEMBRANES FOR THE PRODUCTION OF ULTRAPURE HYDROGEN AND THE RECOVERY OF HYDROGEN ISOTOPES**

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## **1. INTRODUCTION**

The first hydrogen porous metallic membrane was a palladium tube with 1 mm wall thickness which T. Graham<sup>1</sup> used for measuring the hydrogen permeability at different temperatures. His experiments with coal gas showed that the penetrating gas had no odor of coal gas and appeared to be pure hydrogen. Graham forecasted that a quantitative determination of the hydrogen in a gaseous mixture could probably be determined through the hollow cylinder of palladium. Graham<sup>1</sup> measured diffusion rates of hydrogen in palladium and in palladium alloys. It is important to note in Graham's<sup>1</sup> finding that palladium-silver alloy satu-

rated with hydrogen at a low red heat for one hour and cooled slowly in the same gas was not visibly altered and held 20.5 volumes of hydrogen. This alloy later became the first commercially used membrane material for hydrogen extraction from gaseous mixtures.

## 2. HYDROGEN PENETRATION THROUGH PALLADIUM AND ITS ALLOYS

In 1932 C. Wagner<sup>2</sup> stated that the transfer of hydrogen from the gas phase into the Pd lattice involves at least two steps: the dissociative adsorption of hydrogen molecules at the Pd surface and the passage of hydrogen atoms from surface sites into the lattice. Six years later he included<sup>3</sup> an intermediate step in this scheme, i.e. a migration of the chemisorbed hydrogen atoms along the surface until they find a passage to enter the lattice. D. Dobichin and A. Frost<sup>4</sup> investigated the processes of hydrogen adsorption and desorption by measuring the electrical resistance of the Pd films. It was found that desorption of hydrogen in vacuum is not so fast as the hydrogenation of ethylene by hydrogen sorbed in the Pd film. The authors<sup>4</sup> found that the reaction rate is not limited by hydrogen transfer from the lattice to the surface because of different rates of ethylene, butene and acetylene hydrogenation. The other reason for this conclusion was a small influence of the hydrogen concentration in the film on the hydrogenation rate. The admission of a mixture of ethylene and hydrogen into the vessel containing the Pd film resulted in much slower hydrogenation rate compared to hydrogen sorbed in Pd. Hydrogen sorbed in Pd goes into the reaction without desorption into gas phase while the gas phase hydrogen practically did not participate in ethylene hydrogenation. Adsorption of ethylene on Pd depressed the rate of hydrogen adsorption.

Using a thin walled Pd tube with both sides activated by Pd black coating, E. Wicke and K. Meyer<sup>5</sup> showed that the removal of hydrogen atoms from Pd surface by chemical reaction with ethylene or oxygen is faster than the recombination and desorption in vacuum or in argon. It is clear from the linear increase of  $\sqrt{\frac{P_o^*}{j}}$  as function of  $\sqrt{j}$ : where  $j$  is permeation,  $g$ —atom of H / cm<sup>2</sup> sec. The inside hydrogen pressures varied within  $0.01 < P_o < 10$  Torr. The external pressure was kept very low ( $P_x < 10^{-5}$  Torr) by steady evacuation or hydrogen removal by argon flow or by reaction (ethylene, oxygen). It was found an equation

$$\sqrt{\frac{P_o^*}{j}} = K_s \frac{sV_{Me}}{D} \sqrt{j} + \frac{1}{\sqrt{k}}$$

with  $D$ =Fickian diffusion coefficient,  $n_0$ ,  $n_s$ =H/Pd atomic ratio at the entrance and the exit faces of metal foil per g-atom of metal. The diffusion flux  $j$  is suitable

rather small and the hydrogen pressure  $P_o$  at the entrance side rather high. Under such conditions the solution equilibrium is always established on this side and

$$n_o = \sqrt{P_o^*/K_s}$$

where  $K_s$  is Sieverts constant and  $P_o^*$  differs from  $P_o$  by the correction accounting for the deviations from Sieverts law (for details see<sup>5</sup>). At the exit face of the foil the diffusion flux, coming from the lattice, enters the regime of surface kinetics, according

$$\frac{dn}{dt} = kP_{H_2} \frac{1}{1 + Kn} - k' \frac{Kn^2}{1 + Kn}$$

valid in the range of Sieverts' law. The two terms represent the rates of hydrogenation and of dehydrogenation. The denominator  $1 + Kn$  points to a Langmuir-type chemisorption of H atoms, the surface sites of which are moderately occupied under the conditions of measurements. If H atoms from these sites, however, would recombine to  $H_2$  molecules, the denominator would be expected to be  $(1 + Kn)^2$ .

G. Bohmholdt and E. Wicke<sup>6</sup> observed an inverse H/D isotope effect of the permeation through the wall of the Pd tube. These results were confirmed in the NMR studies<sup>7</sup>. The mobility of hydrogen isotopes in palladium increases in the sequence<sup>8</sup> protium, deuterium, tritium, and the corresponding activation energies of diffusion are 230, 206 and 186 meV. The separation factor between hydrogen gas (G) and hydrogen dissolved in the bulk palladium (B) for protium-deuterium mixtures is<sup>9</sup>  $\alpha^{G_B} = 2.41$  at room temperature and the separation factor between liquid water and gas phase hydrogen is  $\alpha^{L_G} = 3.73$ . The product of these values  $\alpha^{L_B} \approx 9$  was obtained experimentally<sup>10</sup> only with palladium black but later the separation factors from 7.7 to 8.2 were found<sup>11</sup> on compacted palladium. The surface (S)-bulk (B) separation for a protium-tritium mixture in palladium hydride is<sup>8</sup> about 20 at 353 K.

H. Conrad, G. Ertl and E.E. Latta<sup>12</sup> investigated adsorption of hydrogen on palladium single crystal surfaces. After Pd (110) surface exposure in hydrogen of 1 Langmuir ( $1 L = 10^{-6}$  Torr·sec) only a single desorption peak appears at a temperature of 373 K. It increases in size with increasing exposure up to 5 L, but remains constant with still greater exposures. However a second broad desorption peak develops, its maximum is shifted towards higher temperatures with increasing exposures. The first peak arises from adsorbed hydrogen whereas the broad second peak is attributed to desorption of species that were originally absorbed in the bulk. These conclusions are supported by the elimination of the LEED pattern of adsorbed hydrogen and the work function decrease after thermodesorption of the first peak. If such sample rests in ultra high vacuum at room temperature for a few minutes the adsorbed layer is again filled by hydrogen back diffusion from the bulk. A subsequently recorded thermal desorption spectrum again exhibits the first peak

at 373 K. The second peak is shifted towards higher temperatures if the period of time between  $H_2$  exposure and thermal desorption is increased. This is interpreted as a more uniform distribution of the dissolved hydrogen to the deeper layer. From the known bulk diffusion coefficient<sup>13</sup> it follows that H atoms diffuse into the bulk a mean distance of about 0.2 mm within 1000 sec. The analysis of the hydrogen adsorption isotherms gives strong evidence that on the Pd (110) surface hydrogen is adsorbed in the atomic state. The work function of the Pd (110) surface increases at hydrogen adsorption by 0.36 eV. This value for the Pd (111) surface proved to be smaller by a factor of 2. A high index palladium surface, indicating terraces with (111) orientation, 9 atomic rows in width, separated by monoatomic steps also with (111) orientation has the work function increase about 0.23 eV after hydrogen adsorption probably because of the presence of more "open" surface atoms as in the case of a (110) plane. The authors<sup>12</sup> supposed that surface atoms at steps might play the role of active centers in catalytic reactions, but their effect on hydrogen adsorption is not fundamentally different from that of the low index (111) plane. The concentration of dissolved H atoms is probably somewhat enhanced within the layers just below the surface. Dissociative adsorption of hydrogen molecules on Pd (111) occurs with no or only very small activation energy.

The last conclusion was doubted because of finding<sup>14,15</sup> that the apparent activation energy ( $E_{app}$ ) for the  $H_2$ – $D_2$  exchange on the Pd/C catalyst increased by 30 kJ/mol as the Pd crystallite size decreased below 2 nm, and over the Pd/mica catalyst  $E_{app}$  increased by 40 kJ/mol as the Pd crystallite size decreased from 2.5 to 1 nm. The authors<sup>14,15</sup> supposed that this increase in  $E_{app}$  was caused by a decrease in the rate of dissociation of the adsorbed hydrogen and deuterium molecules. P. Chou and M.A. Vannice<sup>16</sup> measured the integral heats of adsorption ( $Q_{ad}$ ) for hydrogen on Pd dispersed on a number of oxide supports and found that for crystallite sizes between 3 and 1000 nm  $Q_{ad}$  remained constant at 63 kJ/mol  $H_2$ . However, on crystallites smaller than 3 nm the  $Q_{ad}$  values increased with decreasing size to 100 kJ/mol. This trend is opposite to that assumed by Takasu et al.<sup>14</sup> but it provides a simple explanation for the variations in  $E_{app}$  reported in<sup>14,15</sup>. Using the Langmuir–Hinshelwood model for  $H_2$ – $D_2$  exchange on Pd Vannice<sup>17</sup> showed that the apparent activation energy is equal to the potential energy well associated with the desorption of HD molecules. If adsorption is nonactivated, this desorption energy is equal to  $Q_{ad}$ . Consequently, the increase in the heat of adsorption of approximately 37 kJ/mol for hydrogen on small Pd crystallites would result in a concomitant increase in  $E_{app}$  equal to the 30–40 kJ/mol reported by Takasu et al.<sup>14,15</sup> This explanation is more consistent with the known behavior<sup>12,18</sup> of hydrogen and deuterium on Pd.

Some palladium rich alloys are more permeable for hydrogen than pure palladium<sup>19</sup> including the palladium–silver alloy mentioned in the Introduction proposed by Graham<sup>1</sup>. Series of binary and tertiary alloys have been prepared at A.A. Baikov Institute of Metallurgy (IMet) of the Russian Academy of Sciences (RAS) and investigated for hydrogen permeability and catalytic activity at Russian Uni-

**Table 1.** Relative Coefficients of Hydrogen Permeation (P) of Pure Palladium and Some Palladium Alloys at 773 K.

Alloy Composition, % Mass.								
Pd	Ag	Au	Pt	Rh	Ru	In	Al	$P_{\text{alloy}} / P_{\text{Pd}}$
100	—	—	—	—	—	—	—	1.0
90	10	—	—	—	—	—	—	1.5
80	20	—	—	—	—	—	—	1.6
70	30	—	—	—	—	—	—	1.8
60	40	—	—	—	—	—	—	1.8
95	—	5	—	—	—	—	—	2.0
90	—	10	—	—	—	—	—	2.2
85	—	15	—	—	—	—	—	2.1
80	—	20	—	—	—	—	—	2.0
90	—	—	10	—	—	—	—	1.2
80	—	—	20	—	—	—	—	0.6
95	—	—	—	5	—	—	—	1.4
90	—	—	—	10	—	—	—	0.9
95.5	—	—	—	—	4.5	—	—	1.4
93.5	—	—	—	—	0.5	6.0	—	2.8
68	30	—	—	—	2	—	—	2.2
80	19	—	—	1	—	—	—	2.6
88.7	10	1	0.1	—	0.1	—	0.1	2.4

versity of Peoples' Friendship (RUPF) and at A.V. Topchiev Institute of Petrochemical Synthesis (TIPS) of RAS, all in Moscow. A part of the hydrogen permeability data is presented in Table 1.

Several alloys have twice as large a permeability for hydrogen as palladium. The other advantages of these alloys in comparison with pure palladium are much higher mechanical properties and stability during thermocycling in hydrogen. For example the hydrogen permeability of Pd-Ru alloy is higher than this value of Pd at a ruthenium content of about 4.5 per cent. The long-term strength of this alloy at 823 K after 1000 hr of operation was greater by a factor of 5 than that property of pure palladium<sup>20</sup>. Some of the new alloys were produced by the Russian enterprises in the form of foils and thinwalled tubes for ultra pure hydrogen production and catalytic membrane reactors.

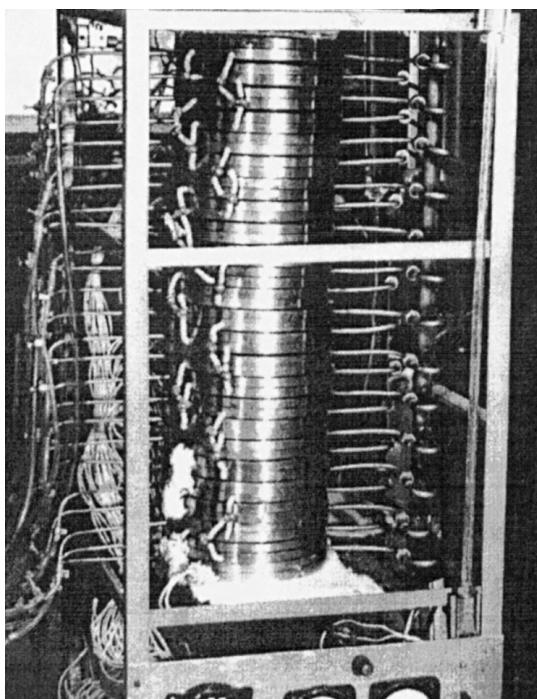
### 3. CATALYTIC REACTORS WITH METAL CONTAINING MEMBRANES

The book "Catalysis by metals and alloys" by V. Ponec and G. Bond<sup>21</sup> begins as follows: "The phenomenon of catalysis as old as life itself: indeed in a very

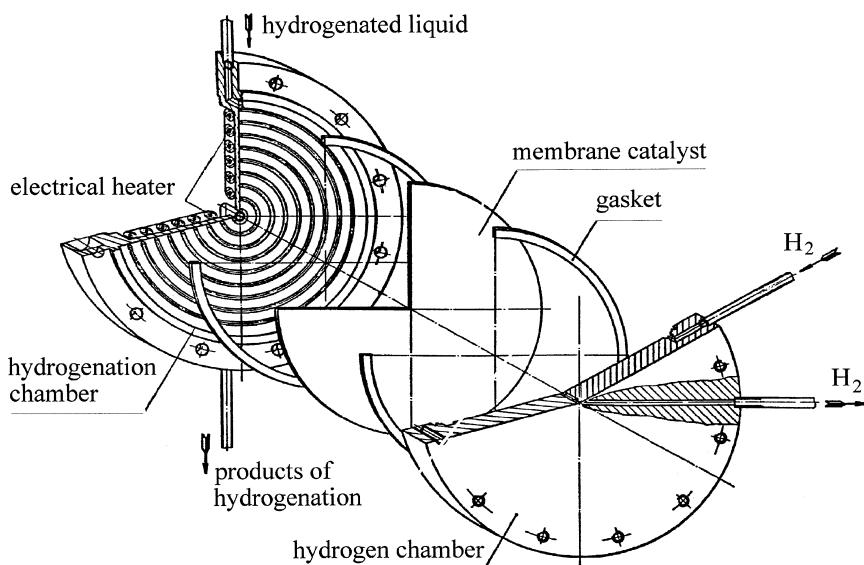
real sense the existence of life is due to enzymatic catalysis. All living organisms are complex catalytic reactors". The similarity of living organism and catalytic reactor increased by the fact of enzymes fixation in the membranes of the cells. It does mean that all living organisms are complex catalytic membrane reactors.

A review<sup>22</sup> summarized the characteristics of many membrane reactors types with palladium-based catalytic membranes in the form of thinwalled tubes and foils. Very durable and easily prepared reactor<sup>23</sup> for liquid phase hydrogenation with flat palladium-indium-ruthenium alloy membranes (Fig. 1) was used as well for obtaining 100 m<sup>3</sup>/hr ultrapure hydrogen from the product of plasmo-chemical pyrolysis of methane and may be recommended for deuterium and tritium recovery from the fuel system of the thermonuclear reactor which is discussed in the next section.

Fig. 2 presents the scheme of one section of the catalytic membrane reactor shown in Fig. 1. The hydrogenated liquid flows in a spiral channel and the products obtained are removed in the center of this chamber. A disc of palladium alloy foil separates the mentioned chamber from the hydrogen chamber of the same construction. Atomic hydrogen penetrates through the palladium alloy foil from



**Figure 1.** Catalytic membrane reactor with flat palladium-indium-ruthenium alloy membranes.



**Figure 2.** The scheme of one section of the catalytic membrane reactor for selective hydrogenation.

the right hand chamber to the left hand one. The discs of foils are hermetically sealed or by copper gaskets deformation or may be fastened by diffusion welding between the two stainless steel shells shown in the schematic of Fig. 2.

The composite membranes with very thin but dense palladium alloy film on refractory porous support are more selective than usual catalysts for production of drugs, eatable hard fats and other substances of high purity. The main advantages of the reactors with composite membrane catalysts in comparison with the reactors containing the monolithic membrane catalyst in the form of foils or thin-walled tubes are higher hydrogen permeability and smaller amount of precious metals. All constructions of the reactors with plane membrane catalyst (see for example<sup>22</sup>) may be used for composites of the thin palladium alloy film and the porous metal sheet. The methods of such membrane catalyst preparation were described in<sup>24</sup>. The hurdles in hermetically sealing of composite membranes into the stainless steel shell of reactors are minimal for the systems on the basis of porous stainless steel sheets. Anodized alumina plate 0.4 mm thick covered with palladium-ruthenium alloy by cathodic sputtering was sealed<sup>25</sup> to the reactor shell with phosphate adhesive. Tubular ceramic supports may be joined with reactor modules through a multiple brazing technique<sup>26</sup>. Until now the junction of composite membrane catalysts to the reactor shell is not so easy and durable as for palladium alloy foils or tubes.

The most general case of catalyst-membrane systems is the system contain-

**Table 2.** The Systems of Metalcontaining Membrane and Granulated Catalysts

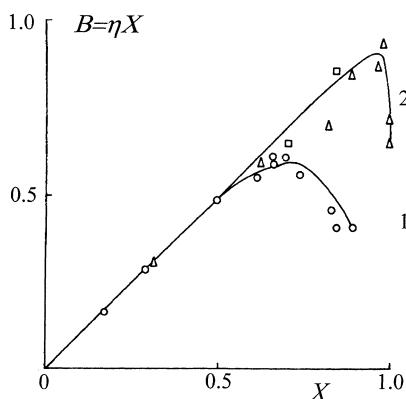
Reaction	Membrane	Catalyst	T,K	Ref
Dehydrogenation of butane to butadiene	Ag, tube	Cr <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	780	27
Methane steam reforming	Pd-23Ag, tube	Ni	723	28
Borneol dehydrogenation to camphor	Pd-10Ru, Pd-10Rh, Pd-5.9Ni, foils	Cu, wire	520	29
Butane dehydrogenation to butadiene	Pd-9.8Ru	Cr <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	723-823	30
Dehydrogenation of cyclohexane to benzene	Pd, tube	Pt/Al <sub>2</sub> O <sub>3</sub>	473	31
Dehydrocyclization of alkanes	Pd-Ag, foil	Zeolite ZSM	723-823	32
Methane steam reforming*	Pd, foil or tube	Ni spheres	1123	33,34
Methane steam reforming	Pd, tube	Pt/Sn,Rh,Ni	400	35
Methane steam reforming	Pd layer on Vycor glass tube	Ni	350-500	36
Dehydrogenation of methyl-cyclohexane to toluene	Pd-23Ag, tube	Sulfided Pt	573-673	37
Ethane dehydrogenation to ethene	Pd-23Ag, tube	Pd/Al <sub>2</sub> O <sub>3</sub>	660	38
Dehydrogenation of isobutane and propane	Pd-Ru or Pd-Ag, tube	Pt/Al <sub>2</sub> O <sub>3</sub>	773	39

\* Reaction in pilot plant

ing a conventional granulated catalyst and a selectively permeable membrane. There are two types of such system: a pellet catalyst with a monolithic or a porous (sometimes composite) membrane. The examples of applications of systems comprising the metalcontaining membrane and the granulated catalyst are collected in Table 2.

Some dehydrogenation reactions were shown to sufficiently intensify over grained catalysts with hydrogen selectively removed through the thermostable membrane. The coupling of the dehydrogenation reaction ( $C=D+H_2$ ) on the grained catalyst and the hydrogenation ( $A+H_2=B$ ) on the membrane catalyst surface proved to be most effective. The experiments were carried out in a plug flow-type membrane reactor with the foil membrane of palladium alloy. The grained dehydrogenation catalyst ( $Cr_2O_3/Al_2O_3$  or  $Pt-Re/Al_2O_3$ ) was placed in one of the chambers where the substance C to be dehydrogenated (butane or cyclohexane, respectively) was supplied in the argon flow at the space velocity  $U_C$ .

Fig. 3 depicts that rising of the  $1/U_C$  value increases the dehydrogenation



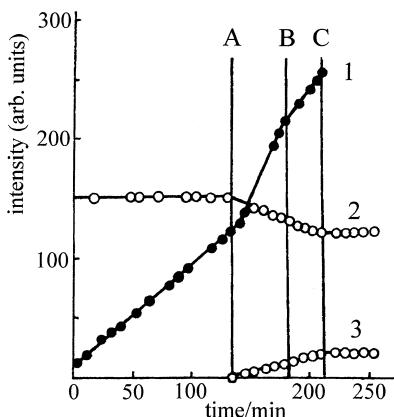
**Figure 3.** Cyclohexane conversion as a function of its reciprocal space velocity at different fractions (d) of hydrogen removal.

rate because of enlargement of the contact time; the higher the more is the degree of hydrogen removal (d) by air flow along the other surface of the membrane. At a d value more than 0.5 the benzene yield from cyclohexane surpasses the equilibrium one (shown by the dotted line in Fig. 3) and at higher degrees of hydrogen removal it is possible to transform cyclohexane into benzene almost quantitatively.

The possibilities of increasing the selectivity of a catalytic reaction by means of one reagent transfer through a septum have been analysed elsewhere<sup>40</sup>. The discharge of hydrogen formed during the dehydrogenation or dehydrocyclization reaction through the hydrogen-porous catalyst raises the reaction rate and the selectivity by suppressing the side reactions<sup>41</sup>. This method is much more effective than a decrease in total pressure or partial pressure of the initial reactants.

Hydrogen introduction through the membrane catalyst into the zone of hydrogenation permits one to control the surface concentrations of hydrogen and hydrogen containing molecules rather independently. It is especially important in obtaining incompletely hydrogenated products that are thermodynamically unstable in the presence of hydrogen. From the academic point of view hydrogen transfer through the membrane catalyst provides an opportunity to elucidate the participation of atomic or molecular hydrogen in the hydrogenation reaction.

The acetylene hydrogenation study shows that ethylene was formed on the outer surface of a tube made of an alloy of 94.1 wt.% palladium and 5.9 wt.% nickel during hydrogen introduction through the tube walls only. Fig. 4 demonstrates that molecular hydrogen input into the glass envelope of the said tube increases the partial pressure of hydrogen (curve 1) but does not change the partial pressure of acetylene (curve 2). Ethylene formation commences immediately



**Figure 4.** Mass-spectral peak intensities of hydrogen (curve 1), acetylene (curve 2) and ethylene (curve 3) against time during acetylene hydrogenation on a palladium-nickel membrane catalyst at 453 K (see text).

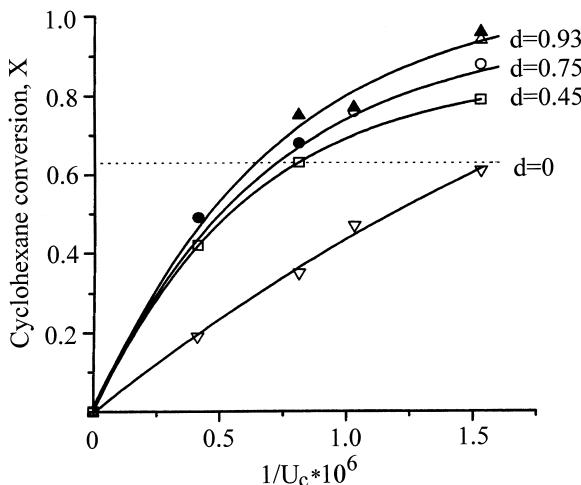
(curve 3) after hydrogen introduction through the tube walls at time A. The cessation of molecular hydrogen input in the glass envelope at time B does not change the rate of acetylene hydrogenation. However, the halt of hydrogen flow through the membrane catalyst at time C stops hydrogenation promptly. These data permit one to conclude that under the mentioned conditions hydrogen in the molecular form does not react with acetylene on the surface of the palladium-nickel alloy membrane catalyst, whereas the hydrogen atoms coming from the sub-surface layer do participate in the hydrogenation of acetylene. The mechanism of acetylene hydrogenation with participation of atomically adsorbed hydrogen has been proposed by G. Bond and P. Wells<sup>42</sup>. In their experiments palladium on an  $\alpha$ -alumina catalyst was very selective for acetylene hydrogenation into ethylene under certain conditions, but the formation of ethane in small quantities suggested complete hydrogenation of a certain proportion of acetylene molecules during one stay on the catalyst surface. Unlike these data, ethane was not detected mass-spectrometrically in the products of acetylene hydrogenation by hydrogen diffusing through the palladium-nickel membrane catalyst. Such high selectivity of hydrogenation may stem from the use of this catalyst in the  $\alpha$ -phase, with a low hydrogen concentration in the alloy. The hydrogen partial pressure inside the palladium-nickel tube was 1 Torr and was thus not high enough for the formation of the hydrogen-rich  $\beta$ -phase. G. Bond and P. Wells<sup>42</sup> mainly used the palladium catalyst in  $\beta$ -phase. A marked increase in the selectivity of acetylene hydrogenation into ethylene after the transformation of the  $\beta$ -phase of the Pd-H<sub>2</sub> system into the  $\alpha$ -phase has been found by Palczewska and coworkers<sup>43</sup>.

The influence of hydrogen concentration in the membrane catalyst on the selectivity of triple-bond to double-bond hydrogenation has been studied<sup>44</sup> by hydrogenation of acetylenic alcohols in the liquid phase on thin-walled tubes made of palladium alloy. The tube was immersed into the liquid and hydrogen was allowed to flow inside the tube. The selectivity of acetylenic alcohol hydrogenation into the corresponding ethylenic alcohol was estimated after the establishment of a stationary reaction rate. The amount of hydrogen dissolved in the membrane catalyst at this time was determined by the amount of acetylenic alcohol hydrogenation products obtained after ceasing the hydrogen supply inside the membrane catalyst. The resulting value differed by less than 5% from the amount of soluble hydrogen in the membrane catalyst found volumetrically. Palladium alloy with a low concentration of the dissolved hydrogen was highly selective towards triple-bond to double-bond hydrogenation. The increase in the amount of dissolved hydrogen decreased the selectivity from 0.9 for the  $\alpha$ -phase to 0.5 for the hydrogen-rich  $\beta$ -phase.

The only product of 2-butyne-1,4-diol hydrogenation by hydrogen diffused through the membrane catalyst during the addition of the first mole of hydrogen was 2-butene-1,4-diol. In contrast to this result bubbling hydrogen through the liquid butynediol in the presence of the same catalyst at the same temperature produced butenediol and butane-1,4-diol from the beginning of the reaction. This again does confirm that hydrogen input through the membrane catalyst makes the hydrogenation process especially selective.

To elucidate the possibility of selective hydrogenation of one ethylenic bond in molecules with two or more double bonds the transformation of cyclopentadiene (CPD) in the vapor phase was studied over palladium-ruthenium alloy. Hydrogen introduction through this membrane catalyst converts CPD into cyclopentene nearly completely<sup>45</sup> (see curve 2 of Fig. 5), although the mixture of hydrogen with CPD vapours yielded less CPE in the hydrogenation products at high conversion (see curve 1 of Fig. 5).

The catalytic membrane reactors applications proposed at Russian University of Peoples' Friendship, A.V.Topchiev Institute of Petrochemical Synthesis and A.A.Baikov Institute of Metallurgy provide the intensification of methane steam reforming<sup>46</sup>, dehydrogenation of butene to butadiene<sup>47</sup>, dehydrogenation of cyclohexane to benzene<sup>48</sup>, dehydrogenation of isopropyl alcohol to acetone<sup>49</sup>. All these processes yield hydrogen that is very pure after the diffusion through palladium alloy membranes. This is why the production of valuable chemicals may be combined with obtaining ultra pure hydrogen. Another advantage of these systems is decreasing the temperature of methane steam reforming and the mentioned dehydrogenation processes with diminished energy consumption and carbon dioxide emission into the atmosphere. Recently catalytic dehydrogenation of propane in hydrogen permselective membrane reactor was studied<sup>50</sup> by the systems with a palladium thin film supported on a porous ceramic support. A propylene yield of



**Figure 5.** Product of selectivity towards cyclopentene  $\eta$  by conversion degree  $X$  plotted against  $X$  for cyclopentadiene hydrogenation in the mixture with hydrogen (curve 1) and during hydrogen introduction through the membrane catalyst (curve 2).

39.6 per cent was obtained compared to a yield of 29.6 per cent in a conventional packed-bed reactor operated at the same flow rate and temperature. In the tube of palladium-ruthenium alloy packed with a supported platinum catalyst 76% isobutene at 773 K was obtained<sup>51</sup> from isobutane compared with 32% in equilibrium. However this yield was limited at low feed rate by suppressed catalyst activity in the absence of hydrogen. Operation under pressure may be advantageous as high purity hydrogen can be produced.

Y. Gokhale, R. D. Noble and J.L. Falconer<sup>52</sup> modelled the dehydrogenation of butane in a membrane-enclosed catalytic reactor. For maximum conversion, they proposed a hybrid reactor with a space time of 0.5 s.

#### 4. HYDROGEN ISOTOPES RECOVERING BY PALLADIUM ALLOY MEMBRANES

The fuel cycle of a thermonuclear deuterium-tritium fusion reactor includes formation of tritiated methane, water, ammonia and other admixtures which have to be separated from deuterium and tritium. Palladium-silver alloy membranes were proposed for hydrogen isotopes recovery from the exhaust gases of fusion reactor. H. Yoshida, S. Konishi and V. Naruse<sup>53</sup> at Japan Atomic Energy Research Institute tested palladium 25 wt. per cent silver alloy tubes 80 micron wall thick-

ness brazed to a nickel tube or disk manifold in the stainless steel shell. Their exposure to methane at 710÷823 K and 134÷382 kPa for 120 hrs didn't change the hydrogen permeability of the membrane, but the oil vapor of the vacuum pump at 713 K depressed the permeability drastically. It can be recovered by air baking for 30 min at 713 K.

The number of palladium-silver tubes 60 sm long in the diffuser is sufficient to purify the gas under the feed conditions of the Tritium System Test Assembly (TSTA) of the Los-Alamos Scientific Laboratory, was numerically and experimentally estimated at 100. The operating temperature of the diffuser was selected as 573 K. In order to reduce the tritium concentration in bleed to 1 per cent, the back pressure of the diffuser is maintained at 0.13 kPa (1 mm Hg). The Fuel Cleanup System (FCS) proposed in<sup>53</sup> includes: a) two palladium-silver alloy diffusers; b) vacuum pumps to transfer the penetrating hydrogen isotopes to cryogenic hydrogen isotope separation process; c) catalytic oxidizer for hydrogen, tritiated methane and ammonia conversion to tritiated water and tritium-free gases. Tritiated water is frozen at 160 K and noncondensable gases are detritiated in the Effluent Tritium Removal System. Tritiated water decomposes at 573 K by zinc beds with formation of zinc oxide and tritium which is flowing through the zinc vapor trap to the second palladium-silver diffuser.

The permeabilities of hydrogen and deuterium through the palladium-25% silver alloy membrane were measured at 800 kPa and 700÷900 K by H. Yoshida, T. Shimizu, Y. Matsuda and Y. Naruse<sup>54</sup>.

Tritium generated in the core of a high temperature nuclear reactor has to be removed from the coolant gas (helium). N. Iniotakis, W. Frohling and C.B. von der Decken<sup>55</sup> at Kernforschungsanlage, Julich (Germany) proposed a tritium filter with helical tube bundle. The only material which will not undergo surface corrosion during the reaction:  $HT + H_2O \leftrightarrow HTO + H_2$  or form hydrides, are palladium alloys. The authors calculated that 2400 kg of palladium-25% silver alloy tubes with wall thickness of 0.4 mm which can be fabricated conventionally would be required for the surface of 500 m<sup>2</sup>. It is mentioned in<sup>55</sup>: "It is possible, however, to construct the tube in such a way that the wall thickness is reduced to 5–20  $\mu m$  while maintaining the mechanical stability of the filter". By this means the amount of palladium required will be reduced 50 times (180 m<sup>2</sup> of Pd-25% Ag foil 20  $\mu m$  thick). The construction of such foil filter is not discussed in<sup>55</sup>.

R.S. Willms and K. Okuno<sup>56</sup> at Los Alamos National Laboratory (USA) developed a membrane reactor for recovering hydrogen isotopes (including tritium) from water and methane. The membrane is a straight Pd-Ag alloy tube 530 mm long with the outer diameter of 5 mm and the wall thickness of 0.2 mm. It was inside the stainless steel shell with the inner diameter of 12 mm. The annular space between the membrane and the shell was loaded with 3.18 mm diameter nickel catalyst for methane steam reforming:  $CH_4 + H_2O \leftrightarrow 3H_2 + CO$  and water gas shift (WGS) reaction:  $CO + H_2O \leftrightarrow H_2 + CO_2$ . With the residence time

chosen properly, full recovery of the formed hydrogen was achieved. R.S. Willms, S.A. Birdsell and R.C. Wilhelm<sup>56</sup> used this reactor for recovering tritium from a mixture of tritiated methane, tritiated water and helium. A stream of ultra pure HT was obtained and a second stream contained helium and carbon oxides.

The hydrogen isotopes flow from the outside of the Pd-Ag tube into its center provides a large volume of catalyst in the annular space between this tube and the reactor shell but the degree of hydrogen recovery is limited by the vacuum at the permeate side of Pd-Ag tube of limited conductance. That is why another reactor configuration<sup>57</sup> was proposed. The catalyst was packed inside the straight Pd-Ag tube with the outer diameter of 3.18 mm, then coiled on a mandrel. Due to the relatively large area of the annular space between this coil and the reactor shell, there was good conductivity and the proper vacuum could be maintained on the permeate side. Since most of hydrogen isotopes are expected to be removed by the membrane reactor of the first configuration, there will be a rather small flow of hydrogen isotopes through the tubes packed with the catalyst, so only a relatively small vacuum system will be required. Initial testing showed that such device recovers hydrogen isotopes from water and methane. However, due to the small diameter of Pd-Ag tube and small catalyst pellets, an excessive pressure drop was encountered on the retentate stream.

Commissioning of the catalytic plasma exhaust clean-up facility and first experimental results obtained at Research Center Karlshure and at Kraftanlagen Heidelberg (Germany) are presented by M. Glugla, R. Kraemer, R.-D. Penzhorn, T.L. Le, K.H. Simon, K. Gunther, U. Besserer, P. Schafer, W. Hellriegel and H. Geissler<sup>58</sup>. The impurities are processed by a combination of methane catalytic cracking  $\text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2$  by the nickel catalyst at 723 K and WGS reaction at 473 K with permeation of hydrogen isotopes through palladium-silver membranes. The design throughput of the facility is 9.6 mol/h DT and 1.7 mol/h tritiated and non-tritiated impurities. WGS reaction was supported by CO formation according to the Boudouard reaction  $2\text{CO} \leftrightarrow \text{C} + \text{CO}_2$ . The carbon deposition rate on the nickel catalyst was calculated to be 0.8 g/h. Authors<sup>58</sup> conclude that the original design specification of the tested facility was fully met.

Palladium-silver alloy used in the studies<sup>53-58</sup> ranks below the mentioned above palladium-ruthenium and palladium-indium-ruthenium alloys in the hydrogen permeability at high temperatures, in the mechanical strength and in the catalytic activity.

## 5. CONCLUSION

Thermostable metalcontaining membranes can be used for separation of hydrogen from products of many industrial processes including dehydrogenation and methane steam reforming with reduced energy consumption and carbon diox-

ide emission into the atmosphere. The waste generation in the processes of selective hydrogenation can be decreased due to higher selectivity of the membrane catalysts in comparison with the conventional catalysts of hydrogenation. Testing of the bench scale membrane reactors for hydrogen recovery from the gases of petrochemical plants and purge gases of ammonia synthesis installations reveal their efficiency in production of ultra pure hydrogen for the semiconductors industry and the space rocket fuel. A membrane reactor was constructed that produces 100 m<sup>3</sup> ultrapure hydrogen per hour from hydrogen containing industrial off-gases and may be used for hydrogenation of liquid plant oils into hard edible fats without cancerogenic fat acids, formed on the usual catalysts active at higher temperatures only.

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