EFFECT OF THERMODIFFUSION AND CHEMICAL TREATMENT OF THE SURFACE OF MEMBRANE CATALYSTS MADE FROM PALLADIUM ALLOYS WITH RUTHENIUM AND RHODIUM ON PENTA-1,3-DIENE HYDROGENATION

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It has been shown that the nature of the metal used for thermal diffusion treatment of the surface of membrane catalysts affects the selectivity toward penta-1,3-diene hydrogenation. The formation of cyclopentene and cyclopentane has been established for membrane catalysts made from Pd Alloys with Ru and Rh that have been subjected to thermal diffusion of Zn and Ga and chemical treatment.

Permeability to hydrogen of membranes made from palladium alloys is increased by the formation of a porous layer on their surface [1]. This suggests that the catalytic properties of the membranes will also be changed.

To investigate the effect of thermodiffusion and chemical treatment of the surface of membrane catalysts we have studied their activity and selectivity in penta-1,3-diene (PD) hydrogenation. Hydrogenation of dienes on Group VIII metals usually results in the formation of just olefins and paraffins [2, 3]. The chief products of PD hydrogenation when hydrogen diffuses through a membrane catalyst made from a Pd/Ru alloy in the temperature range 373-573 K are pentene and pentane [4].

## EXPERIMENTAL

The membrane catalysts were prepared from samples of foil 100  $\mu$ m thick made from Pd alloys with 5.0% by mass Rh (PdRh5) and 15% by mass Rh (PdRh15), and with 5.9% by mass Ru (PdRu6) and 9.8% by mass Ru (PdRu10). Layers of Zn, Cu, Ga or Hg  $\sim$  5  $\mu$ m thick were deposited on their surfaces. Membranes with a Zn layer were kept at 523 K for 1 h, those with Cu at 673 K in an atmosphere of Ar, 3h, and with Ga or Hg at 323 K. Then the Zn was extracted by treating the sample with HCl, the Ga with NaOH solution, Cu with trichloroethanoic acid, and Hg with FeCl<sub>3</sub> solution.

The catalytic experiments were conducted in a double chamber flow reactor with a 24 cm<sup>2</sup> geometrical surface area of the membrane, with  $H_2$  or its mixture with Ar fed in at one side and PD vapor in Ar at the other. The reactor pressure on both sides of the membrane was 0.1 MPa. The initial PD had been purified from traces of sulfur-containing compounds by passing the vapor through a saturated NaOH solution. The products were analyzed chromatographically and from IR spectra.

## RESULTS AND DISCUSSION

Hydrogenation of PD on the membrane catalyst PdRul0 with a roughened surface was studied both after thermal diffusion of Zn and chemical treatment at 1.3 kPa pressure PD vapor and 101.3 kPa H<sub>2</sub> pressure from the input side of the membrane.

As can be seen from Table 1 the main products on the catalyst with a porous surface are pentane, small amounts of pentenes and up to 3.5 mole % cyclopentene and cyclopentane. On the catalyst with a smooth surface the main hydrogenation product is pent-2-ene, as was shown earlier [5].

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1312-1316, June, 1991. Original article submitted May 8, 1990.

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TABLE 1. Variation in PD Hydrogenation Products with Temperature for Original and Zn Treated Membrane Catalyst Made from PdRulO Alloy

Fig. 1. Variation in the selectivity  $(\eta)$  toward pentenes with PD conversion (x) on membrane catalysts made from alloys of PdRul0 (a): 1) with untreated surface; 2) after thermodiffusion and chemical treatment of surface for Ga; 3) for Hg; 4) for Zn; and PdRhl5 (b): 1) with untreated surface; 2') after thermodiffusion and chemical treatment of surface for Cu, and for Pd + Cu alloys: 3) 37.0% by mass Cu; 4) 42.0% by mass Cu.

The variation of the selectivity towards pentenes  $(\eta)$  with conversion (x) for PD hydrogenation (Fig. 1a) shows that the nature of the metal, used for pulverizing the surface, affects the properties of the membrane catalyst. The maximum selectivity towards pentenes is exhibited by samples of processed Ga.

Membranes made from the PbRh15 alloy with surfaces treated by Zn thermodiffusion and chemical extraction gave rise to cyclic hydrocarbons in the catalysate. This was not observed after treatment of the surface with Hg or Cu. The selectivity toward pentenes of the original membrane catalyst made from a Pd/Rh alloy was lower than that of the Pd/Ru catalyst. However after treatment of the PdRh15 surface with Cu the selectivity toward pentenes increased to the level achieved on Pd/Cu alloys, as can be seen from Fig. 1b.

The increase in selectivity of Pd/Rh catalysts could possibly be linked to the formation of new Cu-containing catalytic centers with similar properties to those found on Pd/Cu alloys.

X-ray spectroscopic analysis of the surface layer for membranes made from the Pd/Ru alloy treated with Cu, Zn, Ga, and Hg indicated that up to 40-46 at. % Cu, 5-6 at. % Zn, and 0.2-0.3 at. % Ga remained in the porous layer of the membrane catalyst, but no Hg was detected on the surface. It can be assumed that the Zn and Ga contained in the surface layer form part of the active centers responsible for PD cyclization.

An investigation into the variation in yield of cyclopentene and cyclopentane with temperature for membrane catalysts prepared with Zn and Ga (Figs. 2, 3) showed that the maximum yield of cyclization products for Pd/Ru alloys was observed at 573-603 K. On Pd/Rh alloys treated with Ga the maximum was displaced to the region 600-670 K. The highest maximum of cyclopentene plus cyclopentane was 30 mole % at 573 K on the catalyst made from a Pd alloy



Fig. 2. Variation in the cyclopentene and cyclopentane yields (1, 2) from PD with temperature for the membrane catalyst made from PdRhl5 alloy after surface treatment with: Zn (1, 1'); Ga (2, 2'). PD pressure 13.3 and H<sub>2</sub> pressure 25 kPa.

Fig. 3. Variation in yield of PD cyclization products with temperature for membrane catalyst made from PdRul0 alloy with surface treated with: Zn (1); Ga (2) (continuous line cyclopentane, dashed line cyclopentene). Pressure of PD 1.3-13.3, pressure of  $H_2$  25 kPa.



Fig. 4. PD conversion to cyclopentene and cyclopentane at 573 K for a mixture of  $H_2$  and Ar on the input side of the membrane catalyst made from PdRul0 with surface treated with: Zn (1); Ga (2) (continuous line cyclopentane, dashed line cyclopentene). PD pressure 1.3-13.3,  $H_2$  pressure 25 kPa.

with 9.8% by mass Ru with its surface treated with Ga. Analogous variations in the yield of cyclization products with temperature for PdRh5 and PdRu6 alloys were observed and have not been shown in Figs. 2, 3.

A rise in the partial pressure of PD enables the yield of cyclopentene and cyclopentane to be increased. Thus at 573 K on the membrane catalyst made from the PdRulO alloy treated with Ga the yield of cyclic hydrocarbons increases from  $1.6 \cdot 10^{-5}$  to  $5.2 \cdot 10^{-4}$  mole/(m<sup>2</sup>·sec) on increasing the PD pressure from 0.67 to 26.60 kPa. The degree of conversion to cyclopentene and cyclopentane does not change and is equal to 24.0 and 7.0 mole % respectively, while the degree of hydrogenation to pentenes and pentane decreases from 57.5 and 36.0%. These results were obtained under the optimum conditions for each catalyst.

On the membrane catalyst made from the PdRhl5 alloy treated with Zn an increase in the partial pressure of PD from 0.55 to 17.87 kPa increases the yield of cyclic hydrocarbons from  $0.9 \cdot 10^{-5}$  to  $3.1 \cdot 10^{-4}$  mole/(m<sup>2</sup>·sec) at 573 K. At the same time the degree of conversion to

cyclopentene and cyclopentane remains unchanged and approximates to 15.0 and 4.5 mole % respectively.

An investigation into the effect of diluting the  $H_2$  from the input side of the membrane catalyst with argon on the cyclization process on the PdRul0 catalyst at 573 K showed that as the  $H_2$  was diluted the yield of cyclization products passed through a maximum at a  $H_2$  concentration of 10-25 mole %. When pure argon was fed in from the other side of the membrane catalyst the yield fell to 7-12 mole % (Fig. 4). The process was also suppressed with excess  $H_2$ . When Ar was fed in at the input side of the membrane a large amount of dissolved hydrogen remained in the palladium alloy.

If Ar is replaced by air or mixed with air the cyclization process ceases. In the case of air the hydrogen dissolved in the membrane is oxidized and eliminated from the membrane. These results suggest that there is a certain optimum amount of adsorbed or dissolved hydrogen in the membrane necessary for the cyclization process as well as for the processes of hydrocarbon dehydrogenation and isomerization [6].

It can be assumed that in the first stage during adsorption of the diene it interacts with an adsorbed or dissolved H atom to form an adsorbed complex. Cyclization of this complex results in cyclopentene and on subsequent hydrogenation cyclopentane is formed.

It is apparent that the variation in selectivity of a membrane catalyst treated with Zn, Ga, or Cu is linked to the formation of new active centers. As we demonstrated in [7] a certain amount of Zn, Ga, or Cu remains in the catalyst. These metals are able to form intermetalloids of various compositions with Pd, Ru, and Rh [8]. These intermetalloids are able not only to exhibit hydrogenating properties but can also act as active catalysts for hydrocarbon cyclization.

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