CHANGES IN THE CATALYTIC ACTIVITY AND HYDROGEN PERMEABILITY OF A PALLADIUM-RUTHENIUM ALLOY MEMBRANE CATALYST UNDER THE INFLUENCE OF REAGENTS

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It is well known that structural changes take place on the surface of metals during reactions as well as when the metals are heated above their recrystallization temperature [1-3]. When H₂ and NH₃ are oxidized, or when NH₃ is being decomposed, on Pt, Pd, or Rh, such processes proceed at relatively low temperatures. A restructuring of the surface of Pt wire during the oxidation of carbon monoxide was observed at temperatures <600 K [4]. The formation of facets on the surface of Pt foil as well as the formation of carbon layers containing particles of the metal was observed when oxidizing C_2H_4 over Pt in a temperature interval of 770-970 K [5].

When using deposited and skeletal catalysts, the above described effects increase the dispersion degree of the precious metals and lead to their loss during catalytic processes, a circumstance not typical of membrane catalysts. When working with membrane catalysts, changes in the catalytic activity were observed in a number of reactions over the service time of a catalyst.

The goal of this work was to investigate the effects of the nature of reagents, the temperature of their conversion, and the composition of the environment on the permeability to hydrogen and on the catalytic activity of a membrane catalyst in the hydrogenation of cyclic hydrocarbons and the hydrogenolysis of C_3H_8 .

EXPERIMENTAL

The catalyst used in this work was a Pd-Ru alloy obtained from the corresponding metallic powders (purity \geq 99.8%) by melting them together in a vacuum electrical arc furnace with a tungsten electrode. Based on chemical analysis, the obtained alloy contained: 9.8% Ru, $\leq 0.1\%$ W, the remainder being Pd. Before rolling, the alloy was deformed to ~30%; it was annealed in vacuum and cold rolled to a thickness of 100 µm. Before using the foil in any experiment, it was washed in CCl₄ and acetone, then in EtOH, and distilled water. Before running tests, the catalyst was held for 2 h in an air stream at 723 K, then for 1 h in H₂ at the same temperature. After each experiment, the catalyst was regenerated for 1 h in an air stream at 723 K, and then it was activated with H₂ for 1 h at the temperature of the test.

The hydrogenation and hydrogenolysis reactions were carried out in a continuous circulation reactor. The reaction products were chromatographically analyzed.

RESULTS AND DISCUSSION

In the investigation of the hydrogenation of cyclopentadiene (CPD) and cyclooctadiene (COD) on the membrane catalyst, we found that the conversion of the hydrocarbons and the selectivity toward a cycloolefin changed during the tests. In tests where high CPD and COD conversions were reached, the change in the catalytic activity was less significant than in cases of low conversions.

When conducting a series of experiments, we observed an increase in the catalytic activity from one test to the next. Such "work-up" of the catalyst during the hydrogenation of CPD is shown in Fig. 1, where curves 1-3 show an increase in the conversion of CPD as the number of service cycles (N) of the catalyst increased (one hour test followed by regeneration and activation). The conversion increased from N = 10 to N = 42. The activity drop of the catalyst slowed down during the course of the experiment as N increased leading to a faster establishment of the steady state.

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Fig. 1. Dependence of the conversion of cyclopentadiene on a Pd-Ru membrane catalyst on the duration of the tests. 1-3) At N = 10, 39, and 42, respectively.

Fig. 2. Dependence of the hydrogenation rate of propane at 573 K on τ . 1-7) Correspond to N = 1-7.

Fig. 3. Dependence of the amount of hydrogen diffusing into the hydrogenation zone, into the Ar stream (1) and during the reaction (2), on N.

When hydrogenating 1,5-COD, the reaction rate did not depend on the number of tests conducted with N > 7. When hydrogenating naphthalene, the steady state was reached at N > 9. A comparison of data obtained with a previously used and with fresh Pd-Ru alloy foils showed that the change in the condition of the surface of the catalyst contacted with hydrocarbon vapors and periodically treated with air, increased its catalytic activity toward the hydrogenation of 1,5-COD by over 3 times, and that its selectivity toward cyclooctene decreased from 81 to 65%. The change in the activity and selectivity of samples in the COD hydrogenation process was accompanied by a change in the distribution of isomerization products. While 1,5-COD isomerized to 1,3 and 1,4- isomers on fresh foil, 1,3-COD was not found among the isomerization products with previously used foil. This may be determined by a higher hydrogenation rate of 1,3-COD as compared to that of 1,5- and 1,4-COD; this fact is especially pronounced as the catalyst activity increased.

The growth of the catalytic activity with increasing N was also clearly noticed in the hydrogenolysis of C_3H_8 on Pd-Ru catalyst, as can be seen in Fig. 2. A fresh membrane did not exhibit catalytic activity after 5 consecutive one hour treatments with air at 723 K, and and one hour reduction in H₂ at 573 K did not result in any noticeable conversion of C_3H_8 . Only after one work cycle (N = 1), did the catalyst exhibit a small, but insignificant, activity in the hydrogenation reaction (Fig. 2, curve 1). At N > 1, the activity of the catalyst and the maintenance time of the steady state increased, and at N = 7 the activity of the catalyst reached its maximal activity in the given conditions.

The permeability of the catalyst to hydrogen also changed. Thus, the hydrogen permeability of a fresh membrane amounted to $2.1 \cdot 10^{-3}$ cm³/cm² sec. After the membrane was heated in a stream of air at 723 K and reduced for one hour in hydrogen at the same temperature, the hydrogen permeability remained unchanged. Following N = 2 (1,5-COD), the hydrogen permeability doubled and reached a steady state value. A stabilized hydrogen permeability in a catalyst used in the hydrogenation of isoprene was attained at N > 15. The growth of the permeability to hydrogen of a membrane catalyst was observed up to N = 13 in the case of hydrogenolysis of C₃H₈.

In the course of each catalytic test, the hydrogen permeability of the catalyst decreased; it was, however, restored after regenerating the catalyst in air followed by a treatment in H_2 . As the catalyst was being used for a certain number of N, the H_2 permeability decreased

by different degrees, depending on the hydrocarbon being hydrogenated. Thus, the permeability of a catalyst used to hydrogenate CPD, began dropping after N = 40, and toward N = 50 it decreased to 16%. In contact with COD, however, the hydrogen permeability remained constant up to, and including, N = 70, then it decreased reaching 18% at N = 80.

The total amount of H_2 consumed in the hydrogenation reaction and that remaining in the gas phase did not correlate with the amount of H_2 diffusing into the hydrogenation zone in the absence of the hydrocarbon. During the first five tests with a fresh catalyst, the indicated total amount was below the amount of H_2 supplied to the hydrogenation zone before starting the test (Fig. 3, section I of curve 2), but beginning with N = 6, this total amount surpassed the amount of H_2 introduced into the hydrogenation zone before supplying the hydrocarbon. This is explained, on one hand, by a decrease in the hydrogen permeability of the membrane when replacing argon with a mixture of this gas with the hydrocarbon; and on the other hand, by the increase in the hydrogenation rate from one test to the next. However, the increase in the hydrogenation rate is more important. As a consequence of this, beginning with N = 6 the amount of H_2 transferred to the hydrogenation zone in the course of the reaction surpasses the current of argon in the same conditions (Fig. 3, section II of curve 2). After steady state conditions have been reached in the course of the reaction, more H_2 is always transferred to the hydrogenation zone than into the inert gas stream. The increase in H_2 transfer becomes more significant as the hydrogenation reaction rate increases.

In order to determine the composition of the surface layer on both sides of a Pd-Ru alloy membrane, we used spectra obtained with an AEI ES-100 x-ray photoelectron spectrometer. We have shown that the surface layer of the initial alloy contained 5% Ru. Heating for 5 h at 473 K in Ar had no effect on the composition of the surface layer. A regeneration of the catalyst with air at 723 K followed by an activation in H_2 enriched the surface layer with ruthenium (up to 16%). On the side of the membrane not exposed to the hydrogenation reaction, where the membrane was subjected only to heating to 723 K in Ar atmosphere and to hydrogen treatment, the concentration of Ru increased to 11%. The surface layer of the Pd-Ru alloy, subjected to a periodic influence of the hydrocarbon at temperatures of up to 573 K and to the influence of air at 723 K, contained 27% Ru at N = 50. Micrographs taken with an ISI-60A electron microscope showed that after the hydrogenolysis of C3H8, followed by treatment with air at 723 K, and subsequent reduction in H_2 , the surface, initially smooth, presented a spongy appearance, developed depressions and protuberances. An increase in roughness of the catalyst membrane by 2-3 times under the influence of the dehydrogenation reaction of cyclohexane was shown earlier [6]. Thus, in the course of catalytic reactions with participation of H_2 alternating with oxidative-reductive treatments, profound changes in the structure and composition of the surface layer take place resulting in changes in the catalytic activity and hydrogen permeability.

While catalytic etching has been observed, as a rule, in reactions with the participation of O_2 or in the course of decomposition reactions of NH₃, and was explained by mass transfer via the formation of oxide [7, 8], in the present case the catalytic reaction proceeds in a reductive environment at relatively low temperatures. The structural change of the surface takes place only when the catalytic reaction is being alternated with oxidative-reductive treatments. The oxidative-reductive treatments of themselves change the structure of the surface and the catalytic activity to a much lesser degree. The nature of the reagents influences the formation of the surface structure of the catalyst. Thus, in the course of hydrogenation of COD, the catalyst "work-up" proceeded much faster than when hydrogenating CPD. Apparently, the catalytic corrosion proceeds at the expense of a weakening of the atomic bonds in the surface and subsurface layers of the alloy during the interaction with the adsorbate. It can be expected that the stronger the bonds of the metal atoms with the molecule being adsorbed, the more significant will be the structural rearrangement of the surface. In effect, the adsorbtion coefficient for COD, determined in [9], is 3.6 times higher than that for CPD.

It is also fair to note that cyclic hydrocarbons undergo hydrogenation already on freshly prepared membrane catalysts, but C_3H_8 , which is adsorbed to much lesser degree, begins to be converted only at N > 5.

The adsorbed hydrocarbon-metal complex acquires mobility under certain conditions. This mobility assures the transfer of metal atoms over the surface. Such a system is similar to homogeneous organometallic compounds, but differs in that it preserves its bonding with the lower-lying layers of the metal. Apparently, the mobility of such a system increases when a portion of the metal's atoms is oxidized on the surface. This follows from the fact that the structural rearrangements occurred after the oxidation of the surface of the catalyst. A heat treatment followed by a rapid cooling from temperatures above the recrystallization temperature also increases the activity of the catalyst as a consequence of the creation of super-equilibrium concentrations of catalytically active fault points as was shown in [10, 11].

An important part is played by the gaseous environment and by the condition of the metal during the heat treatment. If a Pd-Ru membrane is first heat treated in air at 723 K and then annealed in an Ar atmosphere at 860 K for $\frac{1}{2}$ h, and then rapidly cooled at a rate of 37 K/sec to the reaction temperature, its catalytic activity in hydrogenolysis of C₃H₈ increases 1.4 times.

If the same treatment is carried out after the catalyst has been saturated with H_2 , its activity in the hydrogenolysis reaction of C_3H_8 drops to zero. This fact also shows that a weakening in the bonds of surface layer atoms by oxidizing them favors the formation of active centers. Galwey et al., and Wu et al. [4, 5] assume the participation of intermediate compounds containing the metal, oxygen, and carbon, in the transfer of metal over the surface.

CONCLUSIONS

1. In the course of catalytic hydrogenation reactions of cyclopentadiene, cyclooctadiene, and isoprene; and in the catalytic hydrogenolysis of propane, all of which proceed at 373-573 K, a catalytic etching of a palladium-ruthenium membrane catalyst is taking place; it is determined by the nature of the reagents.

2. An oxidative-reductive treatment changes the surface structure, the catalytic activity, and the hydrogen permeability to a much lesser degree than when such a treatment is alternated with actual catalytic reactions.

3. A heat treatment followed by a subsequent rapid cooling from temperatures above the recrystallization temperature, increases significantly the activity of a palladium-ruthenium membrane catalyst in the hydrogenolysis of propane.

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