Reconstruction of the surface layer of platinum group metals in the thermal treatment in various gases and propane hydrogenolysis*

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The enrichment with ruthenium of the surface layer of a Pd—Ru alloy tube during the propane hydrogenolysis was observed. Metal particles immobilized within carbonaceous deposits and filamentous crystals of the metals with a carbon cover are formed on the Rh and Ir wires. Thermal treatment in gases free of carbon compounds does not cause such a deep reconstruction. The deep reconstruction occuring during the propane hydrogenolysis is the stronger, the greater the amount of carbon this metal dissolves.

Key words: palladium, ruthenium, rhodium, iridium, catalysts; propane, hydrogenolysis.

Previous studies[1,2] have shown an increase in the catalytic activity of platinum films upon quenching from the recrystallization temperature (T_r). In further studies, the effect of thermal treatment in the medium of various gases on the catalytic activity of the Rh wire in the hydrogenolysis of propane has been investigated.[3] After annealing the wire in an atmosphere of argon, helium, and hydrogen at temperatures <513 K, one C—C bond in the propane molecules is disruptured to form CH_4 and C_2H_6 in equal amounts, while two C—C bonds are disruptured at higher temperatures. The fast cooling of the Rh wire from 1350 K to the temperature of catalysis resulted in a one-order increase in the rate of propane hydrogenolysis as compared with that observed after slow cooling. Under these experimental conditions, ~7% of the fed propane decomposed to hydrogen and carbon, and after treatment of the wire with air at 720 K followed by annealing in argon at 1350 K, 60% of propane transformed to H_2 and carbon.

The purpose of this work is to study the variations in the composition and structure of the surface layers of a Pd—Ru alloy tube and Ir and Rh wires in the thermal treatment and propane hydrogenolysis.

Experimental

A Pd—Ru (6 wt.%) alloy tube of $1 \cdot 10^{-3}$ m outer diameter and wall thickness $1 \cdot 10^{-4}$ m sealed in a plug of the reactor through Kovar joints and rhodium and iridium wires of $2.85 \cdot 10^{-4}$ m diameter attached with screws to the copper buses, were used as the catalysts. The catalysts were heated by a direct current that made it possible to cool them after high-temperature annealing with different rates: either rapidly, by switching off the current source, or slowly, by gradually decreasing the current. The catalyst was one of the shoulders of the Wheatstone bridge that allowed one to heat the catalyst to a specified temperature and simultaneously to measure its resistance to determine the temperature. The propane hydrogenolysis was carried out in a flow-circulation setup at temperatures from 347 to 1123 K and partial pressures of hydrogen in the range of 0—103.8 kPa and those of propane in the range of 0.1—50 kPa. The total flow rate of the reaction mixture was $3.6 \cdot 10^{-7}$ m^3 s^{-1}. The reaction mixtures were analyzed by GC.

The structure of the catalysts surface before and after the experimental runs was studied using ISI-60A and JEM-100 CX11 electron microscopes equipped with an ASID scanning attachment. The metal content in the carbonaceous deposits was estimated on a Camebax MBX-1 instrument with a Tracor detector for the local X-ray spectral analysis.

Results and Discussion

The Pd—Ru alloy tube is inactive in the propane hydrogenolysis even at 773 K both in the original state and after 15 cycles of successive treatment with air and argon at 773 K and with hydrogen at 573 K. Five-fold thermal treatment alternated with the hydrogenolysis runs increased the catalytic activity of the Pd—Ru tube, but the activity rapidly dropped in time; after additional five cycles, the enhanced activity was retained during 45 min. It was found that over the Pd—Ru tube the hydrogenolysis rate can be stabilized in time and the reaction selectivity with respect to methane can be

* Dedicated to the memory of Academician M. E. Vol'pin timed to his 75th birthday.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1100—1103, June, 1998.

1066-5285/98/4706-1067 $20.00

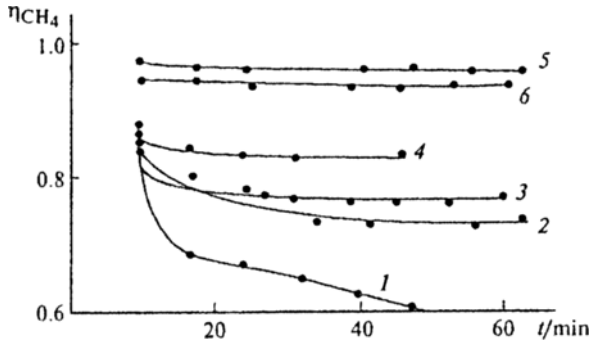

Fig. 1. Time dependence of the selectivity with respect to methane in the propane hydrogenolysis over the Pd—Ru alloy tube at various hydrogen/propane ratios in the feed mixture: H_2/C_3H_8 = 2.7 (*1*), 4.0 (*2*), 6.0 (*3*), 8.0 (*4*), 30.0 (*5*), and 40.0 (*6*).

improved by increasing the hydrogen/propane ratio in the feed. As can be seen in Fig. 1, when the H_2/C_3H_8 ratio is equal to 2.7, the selectivity to methane (η_{CH_4}) decreases from 0.9 to 0.6 during 40 min (curve *1*); at a four-fold excess of hydrogen, the η_{CH_4} value drops to 0.73 and then does not change (curve *2*). A six-fold excess of hydrogen increases the stable-in-time level of η_{CH_4} to 0.75 and an eight-fold excess increases it to 0.82 (curves *3* and *4*, respectively). In the latter case, the rate of hydrogenolysis also did not decrease in time and was the highest among those found at all other hydrogen/propane ratios 40 min after the beginning of the run. With a 30-fold excess of hydrogen, the selectivity to methane was 0.94 and did not change during 45 min (see Fig. 1, curve *5*), but the rate of propane consumption decreased as compared to that observed with an eight-fold excess of hydrogen. With a forty-fold excess of hydrogen, both the rate and selectivity of the reaction decreased (curve *6*).

Thus, conditions are found at which the Pd—Ru alloy exhibits a stable catalytic activity in the propane hydrogenolysis. Methane predominates among the reaction products, and one or two C—C bonds in the propane molecule are ruptured.

As can be seen in the electron micrographs (Fig. 2), the tube lost its metallic luster and a friable layer was formed on its surface after the experimental runs mentioned have been performed. The content of Ru in the surface layer of the tube increased to 11% after 27 h contact with a mixture of reagents at the temperatures from 347 to 628 K. Carbonaceous deposits on the surface of the tube, which are partially carried away by the gas flow, contain Pd and Ru, and the latter is predominantly removed from the alloy in spite of its lesser volatility. When the temperature of the tube is equal to 823 K, the sublimation of the alloy components is observed, although it does not occur even in air up to 1470 K without the catalytic reaction. These facts characterize the high mobility of the atoms at the catalyst

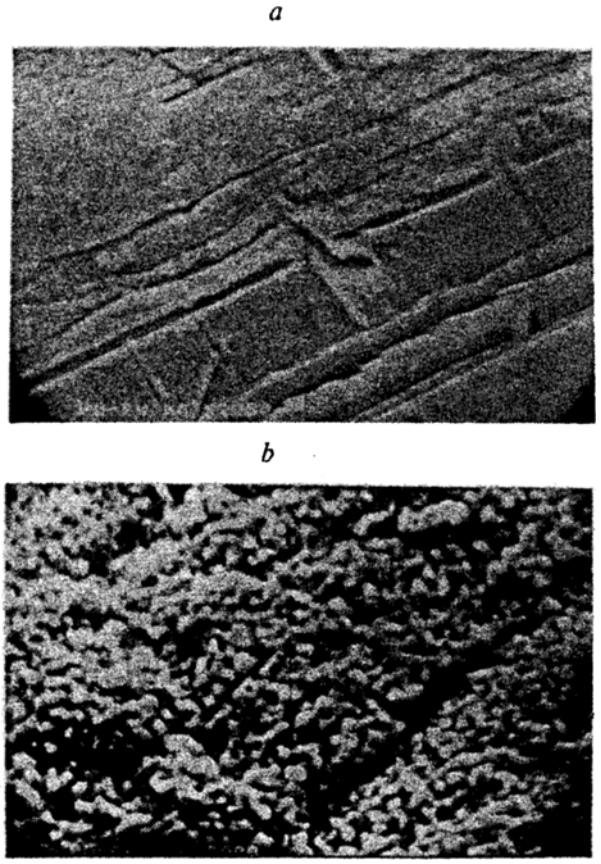

Fig. 2. Electron micrographs of the surface of the Pd—Ru alloy tube before catalysis (*a*) (magnification 2000) and after 27 h propane hydrogenolysis at temperatures from 343 to 627 K (*b*) (magnification 3000).

surface on contacting with the propane molecules and the products of its hydrogenolysis. As the experiments with the Rh wire showed, the products of dehydropolycondensation resulting in the formation of carbonaceous deposits also play an important role in these processes.

The rhodium wire is inactive in the propane hydrogenolysis at temperatures <770 K not only in the original state but also after multiple annealing in air and in the medium of an inert gas at 1100—1300 K. In the quartz tube, 11% of methane, 8% of ethylene, and 3% of ethane were formed from the same propane—hydrogen mixture at 880 K. Hydrogenolysis of propane over the Rh wire was observed only at 915 K ($0.41\,T_m$(Rh)). The ratio between the amounts of methane (5.6%), ethylene (3.1%), and ethane (0.4%) differs significantly from that found for the thermal propane hydrogenolysis. Methane is formed predominantly during the thermal propane hydrogenolysis over the Rh wire. After a series of runs at this temperature, the surface of the Rh wire became friable and filamentous rhodium crystals ~1.5 μ in dia-

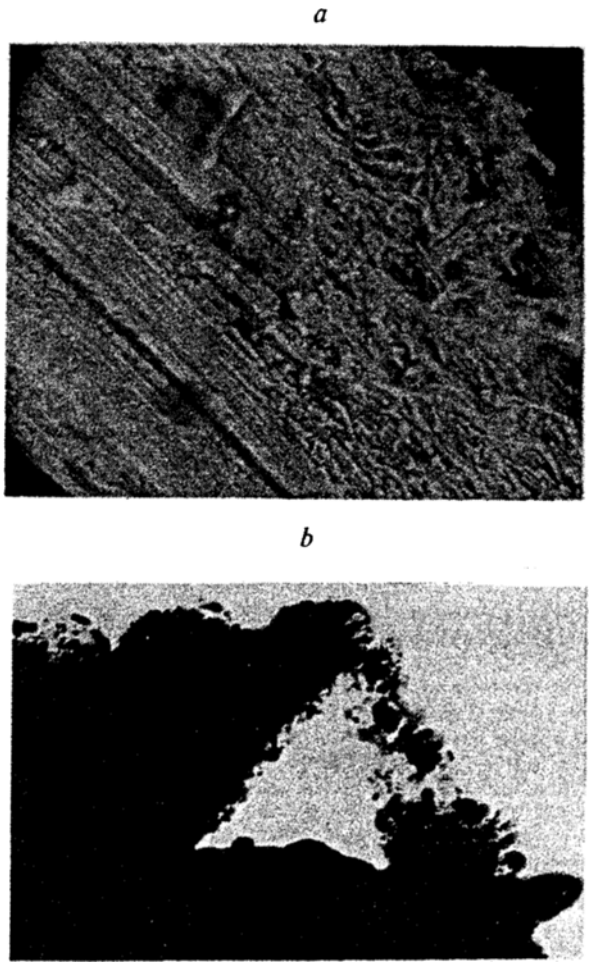

Fig. 3. Electron micrographs of the surface of the Rh wire after the propane hydrogenolysis at 915 K: *a*, obtained with magnification of 300 in the reflection regime; *b*, obtained with magnification of 100 000 in the transmission regime.

meter (Fig. 3, *a*) were formed on it. As a result, the propane hydrogenolysis occurred at lower temperatures. The annealing of the Rh wire in a hydrogen flow for 30 min at 1060 K ($0.47T_m$(Rh)) and cooling to 573 K in one run during 3 s and during 5 min in the other run changed slightly the rate of propane hydrogenolysis. After annealing the wire in an Ar flow at 1350 K ($0.6T_m$(Rh)), the rate of propane conversion over the rapidly cooled catalyst was one order higher than that over the slowly cooled catalyst. The enhanced catalytic activity of the Rh wire after such a quenching was retained for 4 h of the catalyst's operation.

The heating of the Rh wire in air at 1120—1170 K resulted in such an increase in its activity that propane conversion was already observed at 423 K. The annealing at the same temperature proved to be the less efficient, and the annealing in an argon atmosphere at 1350 K ($0.6T_m$(Rh)) increased the rate of propane hydrogenolysis at 573 K, but proved to be insufficient

Fig. 4. Electron micrograph (magnification 100 000) of a part of the layer condensed on the wall of the reactor after a series of runs on propane hydrogenolysis over the rhodium wire.

for achieving the activity of the catalyst at the lower temperatures that is observed after annealing in air.

During hydrogenolysis over the Rh wire, ~7% of propane was decomposed, forming the carbonaceous layer at the catalyst surface. In fact, the activity of the catalyst does not decrease even when the carbonaceous layer becomes visible by eye, because they form islands and then dendrites. The carbonaceous deposits participate in the dispersion of rhodium. The rhodium particles with sizes from 3 to 30 nm covered by the carbonaceous film are seen in the micrograph (Fig. 3, *b*). The outer surface of the larger rhodium particles is also covered by the carbonaceous film which is more transparent for electrons than rhodium.

The contact of rhodium with the propane molecules and the products of its transformations caused the rhodium sublimation at significantly lower temperatures than in air. The portion of the layer formed on the walls of the quartz reactor in which the Rh wire coil was positioned contains pillared rhodium crystals of 3 nm diameter covered with the carbon layer (Fig. 4). Microdiffraction study confirmed the presence of the metal Rh in the sample.

Unlike rhodium and palladium, iridium does not dissolve carbon even at 2000 K. This is most likely the reason why the reconstruction of the surface mentioned above is hampered for the Ir wire. The passing of the propane—hydrogen mixture over the Ir wire at 915 K for 21 h proved to be insufficient for the activation of the wire surface. For example, the propane conversion

at 670 K did not exceed 0.2%. After annealing in an argon flow for 30 min and fast cooling, the rate of propane hydrogenolysis over the Ir wire increased by a factor of 77, and after slow cooling it increased only by a factor of 12. The annealing of the Ir wire in an air flow for 10 min at 1133 K ($0.42T_m$(Ir)) proved to be much more efficient: the rate of hydrogenolysis at 670 K increased by a factor of 708 as compared to the initial rate. Further annealing for 30 min at 1133 K in the air flow and fast cooling increased the propane conversion over the Ir catalyst to 97%; however, its activity decreased during the runs.

The results obtained show that the increase in the catalytic activity of platinum metals in the propane hydrogenolysis is achieved because of the interaction of the surface atoms with oxygen and carbon which results in the dispersion and even sublimation of the metal. Immobilization of the atoms and small groups of the metal atoms within the carbonaceous deposits on the catalyst is also important, because it limits the aggregation of the active sites. The metal-carbon systems thus formed are somewhat similar to the new layered graphite compounds (LGC), the π-complexes of graphite with transition metals including Pd and Ru, which were synthesized and characterized in detail by M. E. Vol'pin and Yu. N. Novikov.[4] Study of the catalytic properties of LGC with one and two metal atoms showed[5] that those transition metal atoms, which are located at the edges of the layer intercalated rather than in the interplanar space, are involved in catalysis. The interaction of the transition metal atoms with the graphite networks provides the transfer of electron density for the system graphite—incorporated substrate molecule—transition metal atom. The introduction of an alkaline metal allows one to enhance the electron density on the transition metal atoms either by direct contact or through the graphite networks.

The rhodium nanoparticles found in this work, which are separated with the graphite-like films, are formed spontaneously from the bulk metal during the catalytic reaction at high temperatures. Their application does not require the inert gas atmosphere that was used,[5] when LCG with transition metals were loaded into the catalytic reactor.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-34109a).

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Received December 15, 1997