ADSORPTION OF C₆ ALIPHATIC HYDROCARBONS
ON Pd–Ru ALLOY

V. G. Dobrokhotov, E. A. Shalvashvili, L. F. Pavlova, and V. M. Gryaznov

The alloy of Pd with 6% Ru is an active and selective hydrogen-permeable membrane catalyst for reactions of hydrocarbon hydrogenation and dehydrogenation [1]. Here we are reporting on a study of interaction of this alloy surface with C₆ aliphatic hydrocarbons with different numbers of double bonds in the molecule (hexane, 1-hexene, and 1,5-hexadiene) and the influence of hydrogen on these interactions.

EXPERIMENTAL

The test unit and procedures described in [2] were used to perform the experiments to study adsorption on the inside surface of a Pd–Ru alloy capillary, using a chromatographic method, based on the exit times of the concentration maxima. The original hydrocarbons and the reaction products were analyzed in a 1000 × 1 mm chromatographic column packed with Chromosorb W (100-120 mesh) with 10% β,β’-oxydipropionitrile, at 303°C with a carrier gas (N₂) flow rate of 1.2 ml/min. "Pure" grade hexane was further purified by distillation; the impurity content was no greater than 0.1%. The 1-hexene that was used contained 3.5% hexane; the 1,5-hexadiene contained no more than 0.5% impurities.

Pulses of hexane, 1-hexene, or 1,5-hexadiene, fed to a capillary with regenerated surface at 303°C with N₂ as the carrier gas, did not give any appreciable uptake of these hydrocarbons due to strong adsorption. For the 1,5-hexadiene, however, we observed a sharp decrease of the retention time (decrease of adsorption) of the subsequent pulses; in order to obtain reproducible retention times, a 2-h nitrogen purge was required between pulses. Analysis of the hydrocarbons leaving the capillary did not show any sort of hydrocarbon conversion on the alloy surface.

Reversible adsorption of hydrocarbon vapors on the Pd–Ru alloy was investigated in the temperature interval 275–360°C, from N₂, H₂, and various nitrogen–hydrogen mixtures.

Isotherms for the adsorption of hexane, 1-hexene, and 1,5-hexadiene vapor from nitrogen at 275°C, of the type shown in Fig. 1, were used to plot hydrocarbon adsorption isobars (Fig. 2); the isobar shape is extremely complex.

In studying the influence of adsorbed and dissolved H₂ on the adsorption of hexane at 303°K, we performed experiments with H₂-N₂ mixtures of various compositions; the results from these experiments are presented in Fig. 3. In these experiments, a mixture of H₂ and N₂ with the given composition was passed for an extended time through and around the capillary; i.e., the alloy was saturated with hydrogen at the given p_H₂. It was shown in [2] that for this alloy at 303°K, up to p_H₂ = 20 torr, the hydrogen-lean α-phase exists; above 30 torr, the hydrogen-rich β-phase is formed. It can be seen from Fig. 3 that in the region of existence of the α-phase, increases in p_H₂ reduce the reversible adsorption of hexane but have the opposite effect in the region of the β-phase.

The experiments with the hexene at 303°K in the presence of H₂ and N₂, even with a hydrogen content as low as 0.25% by volume (p_H₂ = 2 torr), showed that the hexene is completely hydrogenated; only hexane was detected by chromatographic analysis of the products leaving the reactor. In the course of these experiments it was found that the exit time of the hexane that is formed is very much dependent on the length of time that the reactor is purged with H₂-N₂ mixture between hexene pulses. If a pulse follows immediately after the exit of the preceding pulse from the reactor, the hexane obtained from the hexene is adsorbed hardly at all on the alloy surface. When the purge time is extended to 2 h or more, the exit time of the hexane obtained in the reaction becomes close to the exit time of a hexane pulse fed to the reactor under the same conditions. A comparison of the quantity of hexane introduced into the capillary and the hexane leaving the capillary indicated negligibly small absorption of hydrocarbons in the reactor.

After these experiments, the capillary-catalyst was purged for an extended period with nitrogen at 303°K. In the course of this purge, pulses of hexene vapor were fed to the capillary, and the hydrocarbons leaving the capillary were analyzed chromatographically. In Table 1 we have listed the degree of hexene conversion (in %) and the relative reduced retention time t_R^β of hexene and hexane for 2–3 consecutive pulses in the course of such a purge

\[ t_R^β = \frac{t_{max} - t_0}{t_0} \]

where t_{max} is the exit time of the maximum on the hydrocarbon peak; t_0 is the exit time of a nonsorbing gas (in the present instance, CH₄).

It can be seen from these data that the hexene conversion gradually decreases as the hydrogen dissolved in the alloy is removed by the purge and the hydrogenation reaction, and that the hydrocarbon retention time depends almost entirely on the length of the purge between pulses. During such a 2-h purge, the desorbed products were condensed and analyzed. The sole product of the desorption proved to be hexane (7·10⁻⁸ mole, which corresponds to approximately 1% coverage of the surface). After regeneration of the capillary by oxidation and reduction with removal of the H₂ at 650°K, the retention times of hexane and hexene no longer depend on the length of the purge between pulses. Thus, in the process of interaction of hexene and H₂ with the alloy surface, adsorption complexes are formed, lowering the reversible adsorption of hexane and hexene nearly to zero. The catalytic activity of the surface remains the same in this process.