CALORIMETRIC STUDY OF THE INTERACTION OF OXYGEN WITH Pd-BLACK AND Pd/Al₂O₃

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Oxygen on Pd-black is adsorbed in two forms with heats from 89.7 to 20 kcal/mol. It is shown that, upon heating to 100–120 °C, oxygen is dissolved. At room temperature oxygen is adsorbed on Pd/Al₂O₃ with a lower heat than on Pd-black owing to the influence of the carrier on the electronic state of palladium.

The results of oxygen chemisorption studies on Pd-black and Pd/Al₂O₃ catalysts by a microcalorimetric method are reported.

Pd/Al₂O₃ catalysts were prepared via the impregnation of γ-Al₂O₃ with a solution of Na₂PdCl₄, drying at 100–105 °C in air and reduction by hydrogen at room temperature for 6 hrs with subsequent washing from chloride ions. Pd-black was prepared via the deposition of palladium hydroxide from a PdCl₂ solution with subsequent reduction in a hydrogen stream at 28 °C (3 hrs) and washing from chloride ions.

The specific surface of Pd-black and the metal surface of Pd/Al₂O₃ catalysts were measured by oxygen adsorption at room temperature /1/.

The differential heats of oxygen adsorption on Pd-black at 25 °C decrease from 89.7 to 19 kcal/mol, oxygen adsorption being irreversible (Fig. 1). Pd-black was
Fig. 1. Differential heats of oxygen chemisorption on Pd-black. 1, 2, 3 - O₂ adsorption at 25 °C; 4, 5, 6 - additional O₂ adsorption at 100 °C. Portion 6 - O₂ adsorption 15 hrs after portion 5

kept at 25 °C and P₀₂ = 0.1 Torr for 10 hrs, but no additional O₂ adsorption was noted. At 100 °C O₂ chemisorption is fast at first but then slows down. Under these conditions the amount of O₂ sorbed by palladium significantly increases: at 100 °C 11 μmol O₂/m² is adsorbed with q = 85 kcal/mol and 6 μmol O₂/m² with q = 20 kcal/mol, while at 25 °C, 3, 5 and 1 μmol/m², respectively (Fig. 1). The supermonolayer absorption of O₂ at 100 °C may be attributed to its dissolution in Pd crystals, at the same time dissolved oxygen does not affect its chemisorption heat.

During the interaction of O₂ with a metal surface various types of the surface Me-O bond may be formed. The initial heats (89 kcal/mol) probably correspond to a bridged form of adsorbed oxygen.

The heat of PdO oxide formation is 20.4 kcal/mol /2/, while the energy of PdO dissociation is 67±7 kcal/mol /3/. The bond energy of adsorbed oxygen at maximum coverage is 68.5 kcal/mol. Therefore, it may be supposed that the interaction of oxygen with palladium at 25 °C is accompanied by the formation of two forms of adsorbed oxygen: bridged and linear.