ON THE DEPENDENCE OF THE CATALYTIC ACTIVITY OF PLATINUM ON SIZE AND ORIENTATION OF THE CRYSTALLITES

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ABSTRACT

The influence of structural factors upon the activity of platinum catalysts for different reactions was investigated. Processes of electrolytic hydrogen and oxygen evolution, anion and methanol adsorption and methanol oxidation were used as model reactions.

It was shown that for methanol oxidation the catalytic activity of platinized platinum, referred to unit true surface, is appreciably lower, than that of smooth platinum. Investigations on monocrystalline platinum have shown that on different crystal faces the isotherms for hydrogen adsorption are similar. Neither is there a difference as regards the oxygen adsorption isotherm and the kinetics of oxygen and bromine adsorption. However, there is a appreciable change in the rates of methanol adsorption (involving dehydrogenation of the methanol molecule) and of the oxidation of organic residues on the surface. On the (111) face with the greatest density of surface atoms the rate constants (referred to one surface atom) exceed the relevant constants on other faces 3-6 times. An analogous effect can be observed for hydrogen and oxygen evolution. The values of the activation energy remain unchanged, the density of the surface atoms affecting mainly the preexponential factor. Annealing of polycrystalline platinum or preliminary mecanical deformation do not affect the adsorption and catalytic properties of the surface.

On a smooth carbon surface (glassy carbon covered with nonporous pyrolytic carbon) low quantities of platinum microcrystallites were deposited electrolytically. The surface concentration was low enough to prevent overlapping. The hydrogen evolution rate depends on the crystal size and on the mean distance between crystallites on the surface. For small crystallites (i.e. for high specific surface areas) and for small amounts of crystallites on the surface the reaction rate exceeds 5-7 times the rate on smooth platimum.