

HYDROGENATION OF MALEINIC ACID BY HYDROGEN, ADSORBED ON SKELETAL NICKEL CATALYST

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One of essential differences of skeletal catalysts from more other types consists of impurity of not dissolved initial phases rendering influence to their structure, adsorption and catalytic property. It is shown, that in an active layer of skeletal catalyst, to the order with a dispersed nickel, there are Ni₅Zn₂₁ and NiZn layerwise, and both ions of a nickel and zinc in solution are present with full dissolution of an active layer. The structure and state of an active nickel layer determine its high reaction ability. As the zinc dissolved from a surface alloy during preparation of the catalyst not completely and is present in active layer as intermetal Ni,Zn-phases, have made the supposition, that the dissolution of these phases will in much determine regularities not only shaping, but also property of an active nickel.

The work includes stages: study of regularities of dissolution Ni,Zn- alloys, optimization of deriving of the surface skeletal nickel catalyst on nickel (Nissc) from surface Ni,Zn-alloy, research of hydrogen state on a skeletal nickel and experimental confirmation of presence of coupling of partial processes which are flowing past in a system with shaping of the catalyst and in process hydrogenation on Nissc.

Outcomes of a research of properties of hydrogen adsorbed on Nissc and on Ni,Zn-phases (Ni₅Zn₂, NiZn₃ and NiZn), being an initial material for preparation Nissc here are submitted. A reaction of hydrogenation of maleinic acid have chosen as model for study of a state and activity of hydrogen.

The preparing of Nissc is accompanied by intensive evolving of hydrogen and its adsorption on an active nickel. Thus two are defined such as an adsorption of hydrogen: an atomic adsorption displacing a potential of an electrode till -0.35 V in a negative direction, and van der Waals adsorption which is moving a potential in a positive direction. First of all hydrogen is adsorbed atomically on active centers with a higher free energy. At the second time the less active centers become filling also, where the adsorption will be molecular. This hydrogen (probably dissolved or in hydrit) could not go out from a surface of the catalyst without polarization.

For a research of a system Nissc-hydrogen the conditions supporting an equilibrium between Nissc and a gas phase were created. The values of stationary potentials of all phases saturated by hydrogen (Ni, NiZn, NiZn₃, Ni₅Zn₂₁ and Nissc) in 0,1N NaOH was more positive, than at similar, unsaturated by hydrogen. However, after adding in a system 0,01mol/l maleinic acid (MA) solution, the potential saturated by hydrogen electrode did not vary. It is possible, if the hydrogen on a surface is in the inactive form. In too time, the potential unsaturated by hydrogen just preparing

Nissc with adding MA in a working solution has increased on 20-30 mV, and the diminution of concentration MA in a solution was observed. It testifies to presence in a surface layer of hydrogen in active, atomic, condition. With cathode polarization of such electrode (-1V) in 0,1N NaOH + 0,01N MA solution the velocity of reduction of maleinic acid is 53,6 mA/cm² (under the analysis of a solution). In too time, the common cathode current with the same potential (-1V) is 1,7 mA/cm². The velocity hydrogenation MA on saturated by hydrogen nickel in a solution with 1 mol/l MA with a potential -200 mV in one thousand time exceeds a velocity of cathode process. In turn with cathode polarization NiZn₃ the velocity hydrogenation of MA in solutions 0,01-2 mol/l MA (under the analysis of a solution) also on 1-2 order is higher than a velocity of cathode process in the same conditions. Therefore it is possible to assume, that the reduction of MA flows past for the account of active hydrogen on the chemical mechanism, as it happens on Pd.

It was shown, that with anode polarization maleinic acid isn't reduce on a pure nickel. However with anode polarization (-50 mV) NiZn₃ the velocity of reduction of maleinic acid defined on the analysis of a solution is 10- 50 mA/cm². Probably, this process flows past with participation of hydrogen formed with selective dissolution of zinc and adsorbing in a dispersible surface nickel layer.

Thus, during selective dissolution of zinc with forming Nissc and its ionization from not full dissolved intermetal phases, the active nickel layer is sated with adsorbed hydrogen in two basic forms - active (atomic) and inactive (molecular). The active hydrogen is capable to hydrogenate of MA without current and with anode polarization. The inactive hydrogen becomes active only under cathode polarization. The saturation of a skeletal nickel by hydrogen from a gas phase reduces concentration inactive the forms of adsorbed hydrogen.