CATALYTIC PROPERTIES OF PLATINIZED POLICYANOGENS

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The effect of various inorganic polymers on the catalytic activity and selectivity of platinum in the hydrogenation of 4-chloronitrobenzene and dinitrotoluene has been studied. Platinized iron-containing polycyanogens are less active but more selective catalysts for the hydrogenation of 4-chloronitrobenzene than Pt/C or Pt/BaSO₄.

Исследовано влияние различных неорганических полимеров на катализитическую активность и селективность платины в гидрогенизации 4-хлорнитробензола и динитротолуола. Платинированные полицианогены, содержащие железо, являются менее активными, но более селективными катализаторами гидрогенизации 4-хлорнитробензола, по сравнению с Pt/C или Pt/BaSO₄.

The main problem of the catalytic hydrogenation of chloro-substituted aromatic nitro-compounds to chloroanilines is in dehalogenation. In case of the most convenient catalyst, Pt/C, the change of the solvent [1], the pretreatment of the catalyst or addition of P-, S- or N-containing compounds [2-5] suppressed dehalogenation below 0.1 %.

Now, we report how inorganic polymers having conjugated -C=N- bonds influence the catalytic activity and selectivity
of platinum in the hydrogenation of dinitrotoluene and 4-chloronitrobenzene.

EXPERIMENTAL

Preparation of the inorganic polymers is given in the footnotes to Tables 1 and 2. The polymers of C and BaSO₄ were platinized by precipitation of a Pt-sol by NaCl [6]. Catalysts prepared in this manner contain 0.37 % of platinum.

Hydrogenation experiments were carried out with a gas burette at constant pressure, 30°C and 0.1 MPa total pressure. The reactions were started by addition of deoxygenated methanolic solution (1 cm³) of the substrate to 20 cm³ of methanol containing the catalyst under hydrogen. The amount of the absorbed hydrogen was determined gas-volumetrically, the concentration of 4-chloronitrobenzene and 4-chloroaniline was followed by gas chromatography. For GC measurements, a CHROM-5 gas chromatograph with 5 % SE-54 Gas Chrom Q column was used.

RESULTS

Data in Tables 1 and 2 show that the platinized inorganic polymers have lower catalytic activity than platinum on C or BaSO₄. However, the activity of the platinized polycyanogens containing iron or cobalt was higher than that of platinum on polycyanogen.

According to detailed kinetic investigations, the rate of the catalytic hydrogenation is proportional to the amount of catalyst, and follows a saturation-type curve with the substrate concentration.

The reaction rate was considerably lower in ethanol, i-propanol and n-amyl alcohol than in methanol. It should be noted that the reaction needs methanol of high purity, and in the case of "reagent grade" methanol we did not observe any hydrogen sorption.

Figure 1 shows the change of the concentrations of 4-chloronitrobenzene and 4-chloroaniline during the hydrogena-