

PREPARATION AND INVESTIGATION OF SELECTIVE METAL- AND METAL-COMPLEX/ACTIVE CARBON CATALYSTS FOR HYDROGENATION

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Introduction

Active carbon (AC)-supported catalysts based on noble metals or their complexes have been widely used for industrial applications. Immobilised metal-complex catalysts, as a rule, combine advantages of homogeneous and heterogeneous catalysts [1,2].

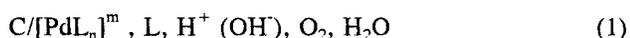
Electrochemical, physical and chemical properties of AC's play a very significant role in their widespread and increasing use as adsorbents and catalysts supports [3]. This is specially important when the AC supported catalysts are prepared by adsorption of metal ions from liquid phases.

The objectives of present work are:

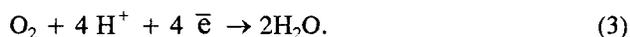
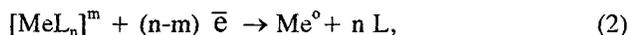
- creation of new method for preparation of AC-palladium catalysts which is based on the reductive sorption processes (ability of AC's to reduce partly or completely the noble metal ions adsorbed onto their surface) [4];
- preparation of palladium catalysts supported on synthetic AC's for hydrogenation in solutions;
- determination of correlation between chemical state of palladium on catalysts, porous structure of carriers and activity of prepared catalysts in liquid-phase reactions of phenylacetylene (PA) and butadiene-nitrile rubbers (BNR) hydrogenation.

Model of Reductive Sorption

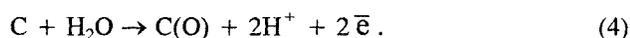
In the system:



two cathode-bound reactions can occur on AC:



These reactions are conjugated to the oxidation of AC matrix:



Reactions of the type (2) are thermodynamically favourable in the system (1) provided their equilibrium potential is more positive than the potential of the AC surface: $\Delta E = E([MeL_n]^m/Me^0) - E(AC) > 0$.

Reaction (3) plays an important role in the system (1) as it determinates the rate of the potential formation on the surface of AC and its value [5,6].

In contact with solution, the potential of the AC surface grows from the initial value to the stationary value (E_{st}). For each type of AC these potentials are dependent on the pH of the solution; increase of pH causes shift of the potentials to the negative side of the scale. In course of the reaction (2) and (3) the E_{st} of AC surface changes in the wide range of values due to the oxidation of the AC's surface by reaction (4). In the presence of Cl⁻ anions palladium is reduced to the metallic state and precipitated on the surface of AC. In contrast, the potential of the oxidised AC surface decreases in contact with the hydrochloric solution and remains higher than the potential of the couple $[PdCl_4]^{2-}/Pd^0$, which makes the reduction of palladium to the metallic state thermodynamically unfavourable.

Stationary potential of Pd reduction from its complex cation with ammonia is negative on the hydrogen scale but E_{st} of AC is positive in these conditions, therefore, Pd cannot undergo electrochemical reduction on the AC surface.

Experimental

Synthetic AC's prepared from polymer-pyrolysed resin (carbons type SCN and SCS) and their oxidised forms were used as catalyst carriers [7]. The porous structure of the carriers was studied by mercury porosimetry and nitrogen adsorption at 77 K. Application of palladium to AC's was carried out by adsorption from solutions: $PdCl_2 + HCl$ (pH=0-2), $Pd(NO_3)_2 + HNO_3$ (pH=1) and from solutions of $PdCl_2$ in aqueous ammonia (pH=10-11) at 25°C [2]. The valence state of Pd on the carbon surface was determined by XPS method [5,6]. The activity of supported catalysts were studied in model liquid-phase reactions of PA and BNR [7] hydrogenation.

