

Introduction

Modern environmental standards in industry dictate the need to revise obsolete technologies, to create energy and resource-saving processes.

Catalytic oxidation and reduction reactions, one of which is selective hydrogenation of long-chain alkynols, are widely used in fine organic synthesis and petro chemistry. Hydrogenation of acetylene compounds is one of the major stages in synthesis of pharmaceuticals, odorants and biologically active compounds [1-4]. In industry such processes are usually carried out over homogeneous catalysts under strict conditions with high yield of by-product. This complicates the technological scheme, since it is required to carry out operations of catalysts and target products separation.

In this regard, the design of new, environmentally friendly catalytic systems with better performance for acetylene compounds hydrogenation is of great importance. Study of literature has shown an extremely high interest of researchers to the development of new types of catalysts based on advances in nanochemistry [5-7]. Such approach makes it possible to form catalytic systems with predetermined properties, capable of carrying out organic syntheses under mild conditions, with high yields of target products and performing high selectivity and activity over a long period of use [8-11]. One of the methods of obtaining such catalysts is stabilization of nanoparticles by organic compounds and soluble polymers [12, 13].

Due to their structure and the presence of various functional groups high-molecular compounds interact with metals forming polymer-metal complexes (PMC), which perform high activity and selectivity at low pressures and temperatures in many hydrogenation and oxidation reactions [14]. At the same time, such systems are relatively unstable, and the presence of polymer ligands introduces new properties to catalysts, such as the flexibility and mobility of segments of polymer chains, as well as swelling, which limits their large-scale application and requires a revision of instrumental design of the processes [15].

The fixing of polymer-metal complexes on inorganic carriers leads to a decrease in the degree of swelling, increases the stability and selectivity of catalysts, provides the formation of active phase nanoparticles [14, 16]. However, factors that affect the formation of nanoparticles, their uniform distribution on the support and behavior in catalytic processes remain poorly understood, which makes it very difficult to create catalytic technologies based on them. In this regard, research on the construction of supported nanocatalysts modified with high-molecular compounds is of high importance.

In the present work heterogeneous catalysts with uniform distribution of nanosized palladium particles on support's surface were obtained by method of irreversible adsorption of widely used soluble polymers - polyethylene glycol (PEG) and polyvinylpyrrolidone (PVPD) by inorganic oxide (ZnO) and subsequent interaction of supported macromolecules with metal ions. Properties of supported heterogeneous catalysts depend on structure and sizes of metal particles [17, 18]. Polymer-modified catalysts have characteristics of both usual catalysts and polymer-metal complexes (swelling, flexibility of polymer chains). Synthesized catalytic systems perform high activity, selectivity and stability in hydrogenation of unsaturated organic compounds.

Methods of Study

Polymer containing palladium catalysts were synthesized by treatment of zinc oxide with water solutions of polymers and then with palladium chloride solution. Soluble polymers polyethylene glycol (PEG) and polyvinylpyrrolidone (PVPD) were used as modifiers of inorganic support. For comparison catalyst was prepared by treatment of zinc oxide with palladium chloride solution without modification by polymer. Obtained systems were dried in the air and then used in catalytic hydrogenation. The developed catalysts were studied with methods of IR-spectroscopy, electronic microscopy and XPA.

Hydrogenation was carried out over 0.05 gram of designed catalysts under mild conditions ($T = 50^{\circ}\text{C}$, atmospheric pressure of hydrogen) with water and ethanol as solvents. The volume of 3,7,11-trimethyldodecin-1-ol-3 (0.58 ml) was taken from the calculation for the uptake of 100 ml of hydrogen.

Reaction products were analyzed chromatographically in the column filled with a 10% Apiezon-L + 2%PEG-20M phase on Chromaton-N-AW-DMCS. Argon was used as the carrier gas.

Results and discussion

Synthesized catalysts were tested in hydrogenation of 3,7,11-trimethyldodecin-1-ol-3 (C_{15-in}) and 3,7,11,16-tetramethylhexadecin-1-ol-3 (C_{20-in}) to 3,7,11-trimethyldodecan-1-ol-3 (C_{15-an}) and 3,7,11,16-tetramethylhexadecan-1-ol-3 (C_{20-an}).

The most important products of these reactions are 3,7,11-trimethyldodecen-1-ol-3 (C_{15-en}) and 3,7,11,16-tetramethylhexadecen-1-ol-3 (C_{20-en}) which are used in synthesis of biologically active compounds.