

of hydrocarbons [12–15]. In natural oxygenates hem-iron complex of protoporphyrin plays the role of active center. The iron-porphyrin complex is similar to the complex found in oxygen carriers, hemoglobin and myoglobin, as well as in catalase and peroxidase enzymes.

The increased catalytic activity and selectivity of enzymes initiated research aimed on the development of highly efficient catalysts that act like biocatalysts [16-18].

Polymer-metal complexes exhibit high activity and selectivity in oxidation processes. A very promising is use of synthetic nitrogen-containing polymers, which easily form complexes with metal ions, to create catalytic systems [19]. To increase stability with repeated use of catalytic systems, polymer-metal complexes are applied on organic or inorganic supports [20, 21]. Such systems in many cases combine the advantages of both homogeneous and heterogeneous catalysts [22].

Despite the good catalytic properties of polymer-metal complexes on inorganic supports in various processes of organic synthesis, there are very few studies on their characteristics and use in cycloalkane oxidation reactions. Therefore development of new heterogeneous catalysts based on soluble polymer-metal complexes is of great interest for the processes of cyclohexane oxidation.

To create catalytic systems it is preferable to use nitrogen-containing polymers that easily form complexes with metal ions. One of them is water and ethanol soluble polymer of N-vinylpyrrolidone - polyvinylpyrrolidone (PVP). PVP is highly hydrophilic, has a clear tendency to form complexes and good adhesive properties [23, 24]. Among the important properties of this polymer is its non-toxicity.

Catalytic activity of polyvinylpyrrolidone-ferrocyanide complexes fixed on inorganic supports is investigated in the present work. The effect of acidic properties of carrier surface on selectivity of cyclohexane oxidation is studied.

Methods

Polymer-ferrocyanide catalysts were prepared by adsorption method based by deposition of 5% of the active phase on substrate mass. Aluminosilicates (Siral-40 with content of SiO₂ 40% and Siral-20 with SiO₂ content 20%), SiO₂ and γ -Al₂O₃ were used as carriers. Polyvinylpyrrolidone with a molecular weight of 15,000 was used as a macromolecular modifier.

To assess the effectiveness of poly-N-vinylpyrrolidone-ferrocyanide catalyst in oxidation reaction twice distilled chemically pure cyclohexane was used. Purity of substrate was checked by method of chromatography and according to the refraction index. Concentration of substrate in the experiments was $2.7 \cdot 10^{-3}$ mole/l. 40% solution of hydrogen peroxide was used as oxidizing agent. As a solvent it was used twice distilled chemically pure acetonitrile.

An aqueous solution of polyvinylpyrrolidone containing 0.0522 g of polymer in 5 ml of water was added to the aqueous suspension of carrier (0.5 g of oxide or aluminosilicate in 5 ml of water) at room temperature with constant stirring. Mixture was stirred by magnetic stirrer for 2 hours, after that water solution of potassium ferrocyanide (0.1728 g of salt in 5 ml of water) was added. The resulting system was vigorously stirred for 3 hours, and then left in the mother liquor for 10 hours. The precipitate was washed with a 10-fold volume of water, dried and stored in air at room temperature.

Cyclohexane oxidation was carried out in a laboratory unit (Fig. 1) under mild conditions: at 40 °C and atmospheric pressure.

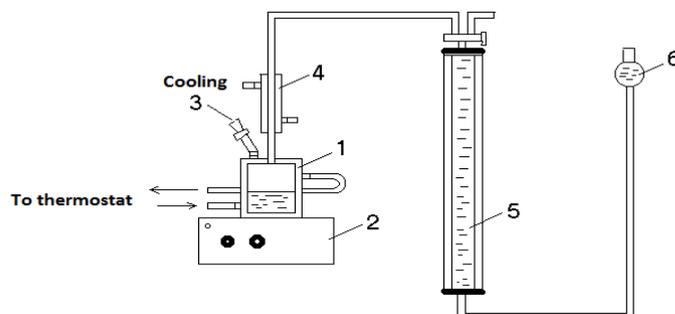


Figure 1 - Volumetric oxidation unit: 1 – thermostatic reactor, 2 – magnetic stirrer, 3 – oxidizer dosing device, 4 – cooler, 5 – measuring burette, 6 – equalizer