**L.K. Tastanova[1], A.K. Zharmagambetova[2],
R.O. Orynbassar[1], A.K. Apendina[1], A.K. Zhumabekova[2]**

[1] K. Zhubanov Aktobe Regional State University, Aktobe, Kazakhstan;
[2] D.V. Sokolskii Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan
lyazzatt@mail.ru, zhalima@mail.ru, raihan_06_79@mail.ru, k.ajnagil@mail.ru, araijk@mail.ru

POLYVINYLPYRROLIDONE-FERROCYANIDE CATALYSTS FOR CYCLOHEXANE OXIDATION

Abstract. Catalysts for cyclohexane oxidation are developed. Polymer-ferrocyanide catalysts fixed on various mineral supports are prepared by the adsorption method. Properties of synthesized catalysts are studied in cyclohexane oxidation with hydrogen peroxide. Reaction is carried out under mild conditions: at 40 °C and atmospheric pressure. All prepared polymer-metal catalysts supported on inorganic substrates are active in the process of cyclohexane oxidation.

Polymer-metal complex fixed on alumosilicate Siral-20 shows 14% more activity than the system fixed on Siral-40. However selectivity of catalyst 5% $K_4[Fe(CN)_6]$ -PVP/Siral-40 is much higher. Under equal conditions, its selectivity for cyclohexanone is 83.4%, whereas selectivity for cyclohexanone of 5% $K_4[Fe(CN)_6]$-PVP/Siral-20 is only 61.7%. Catalyst fixed on γ-Al_2O_3 demonstrates less activity (25.5%) and selectivity than aluminum silicates (cyclohexanone : cyclohexanol ratio is 1.2 : 1). At the same time, with a sufficiently high selectivity for cyclohexanone (70.4%), 5% $K_4[Fe(CN)_6]$-PVP/SiO_2 shows the conversion which is only 17.2%.

The effect of acidic properties of carrier surface on selectivity is studied. It is established that the nature of support (acidic properties of surface) has a significant effect on activity and selectivity of synthesized catalysts.

Polyvinylpyrrolidone-ferrocyanide complex 5%$K_4[Fe(CN)_6]$-PVP/Siral-40 exhibits the best catalytic properties. The conversion of cyclohexane is 42.9%, selectivity for cyclohexanone is 83.4% and cyclohexanone : cyclohexanol ratio is 5: 1.

Key words: polyvinylpyrrolidone, ferrocyanide catalyst, cyclohexane, oxidation, cyclohexanol, cyclohexanone, selectivity.

Introduction

Liquid phase cyclohexane oxidation is an industrially significant process [1,2]. Partial cyclohexane oxidation products - cyclohexanol and cyclohexanone - are used to produce caprolactam, adipic acid, polyamide fibers, nylon-6 and nylon-66 [3,4].

In industry cyclohexane is oxidized by atmospheric oxygen over homogeneous catalytic systems at high temperatures and pressures using toxic solvents. Cobalt, copper, and manganese salts are used as catalysts [5]. At temperatures above 423 K and oxygen pressure up to 3.0 MPa conversion of cyclohexane is 4-15%, selectivity for the sum of cyclohexanone and cyclohexanol is 80–85% [6]. It is quite difficult to carry out reaction of cyclohexane oxidation selectively to cyclohexanol and cyclohexanone which are intermediate products [7-9] of the process.

Selectivity of cyclohexanol and cyclohexanone formation decreases as the degree of initial substance conversion into products rises, therefore in industrial processes in order to increase selectivity it is required to strictly control conversion. In this regard, increasing selectivity of cyclohexanol and cyclohexanone formation with increase in conversion of cyclohexane is a very important challenges of catalysis [10,11].

The problem of saturated hydrocarbons oxidation is associated with high energy consumption for C – H and C – C bonds breaking. In nature reactions of various hydrocarbons oxidation easily proceed with participation of enzymes capable to oxidize with high activity and selectivity non-activated C – H bonds