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Д.В.Сокольский атындағы «Жанармай,  
катализ және электрохимия институты» АҚ

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## ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК  
РЕСПУБЛИКИ КАЗАХСТАН  
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## NEWS

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## **POLYVINYLPIRROLIDONE-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 aluminosilicate 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  $\gamma-Al_2O_3$  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<sub>2</sub> 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

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 SiO<sub>2</sub> 40% and Siral-20 with SiO<sub>2</sub> content 20%), SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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.

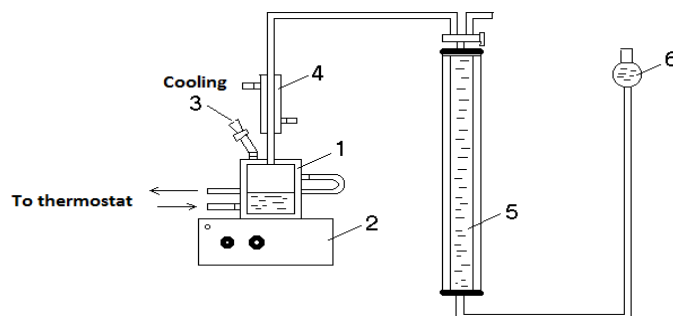


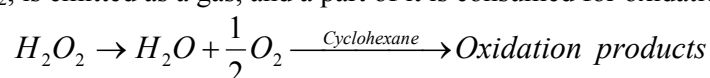
Figure 1 - Volumetric oxidation unit: 1 – thermostatic reactor, 2 – magnetic stirrer, 3 – oxidizer dosing device, 4 – cooler, 5 – measuring burette, 6 – equalizer

A portion of catalyst (0.03 g) was introduced into the reaction vessel with 1.2 ml of acetonitrile. Next, cyclohexane (0.3 ml) and hydrogen peroxide were introduced in the form of 30% aqueous solution, taken in threefold excess with respect to substrate. The reaction mixture was stirred with magnetic stirrer. Oxidation was carried out at 313 K and atmospheric pressure. Reaction mixture was analyzed chromatography after certain periods of time. The amount of released oxygen was determined by volumetric method.

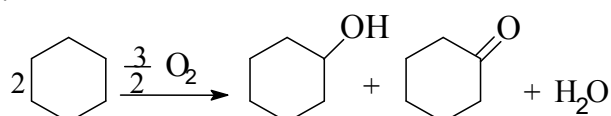
Cyclohexane and products of its oxidation were analyzed by LHM-80M chromatograph with flame ionization detector in isothermal mode. Stainless steel column with length of 3 m and internal diameter of 3 mm was filled with N/W-DMCS chromaton with active phases of 15% Apiezon-L and 3% Carbowax-20M.

### Results and discussion

Synthesized catalysts were studied in reaction of cyclohexane oxidation with hydrogen peroxide. Cyclohexane oxidation is carried out according to the scheme below. Oxygen, which is formed during decomposition of  $H_2O_2$ , is emitted as a gas, and a part of it is consumed for oxidation of cyclohexane:



Formation of oxygen-containing compounds – cyclohexanol (-ol) and cyclohexanone (-one) takes place according to reaction:



Calculated amount of oxygen required for oxidation of 1 mole of cyclohexane is 0.75 mole. The results of cyclohexane oxidation on synthesized systems are presented in Table 1.

Table 1 - Yield of cyclohexane oxidation\* with  $H_2O_2$  products on catalysts 5%  $K_4[Fe(CN)_6]$ -PVP/support

| Catalysts                                       | Reaction products, % |      | Conversion, % | Selectivity, % |      |
|---|----------------------|------|---------------|----------------|------|
|   | -ol                  | -one |               | -ol            | -one |
| 5% $K_4[Fe(CN)_6]$ -PVP/Siral-40                | 35,8                 | 7,1  | 42,9          | 83,4           | 16,6 |
| 5% $K_4[Fe(CN)_6]$ - PVP /Siral-20              | 30,9                 | 19,2 | 50,1          | 61,7           | 38,3 |
| 5% $K_4[Fe(CN)_6]$ - PVP / $\gamma$ - $Al_2O_3$ | 13,7                 | 11,8 | 25,5          | 54,9           | 45,1 |
| 5% $K_4[Fe(CN)_6]$ - PVP / $SiO_2$              | 12,1                 | 5,1  | 17,2          | 70,4           | 29,6 |

\* Reaction conditions: solvent – acetonitrile, T = 313K, P = 1 atm.

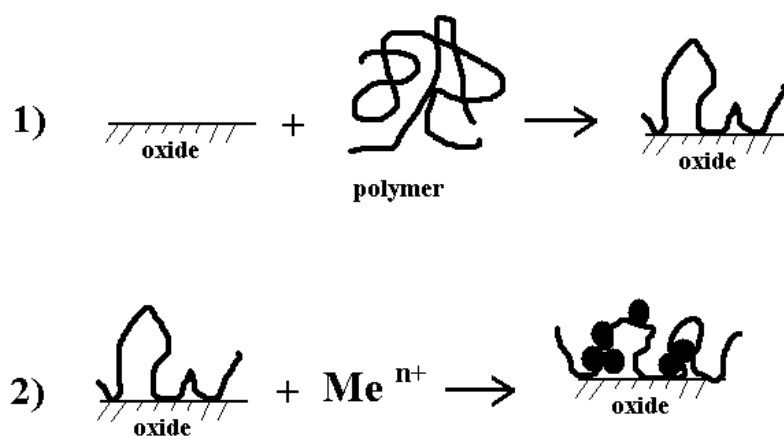


Figure 2 - Scheme of supported polymer-metal complex formation



As can be seen from the data in table, despite the fact that the polymer-metal complex fixed on Siral-20 shows 14% more activity than the system fixed on Siral-40, selectivity of the latter is much higher. Thus, on 5%  $K_4[Fe(CN)_6]$ -PVP/Siral-40 catalyst, selectivity for cyclohexanone is 83.4%, whereas for polymer-metal complex fixed on Siral-20 it is only 61.7%. Catalyst supported by  $\gamma-Al_2O_3$  shows 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%) on 5%  $K_4[Fe(CN)_6]$  - PVP/SiO<sub>2</sub>, conversion is only 17.2%.

Apparently, high selectivity for aldehyde of the process on catalyst supported on Siral-40 is associated with formation of active centers with participation of polymer ligands that contribute to the specific orientation of substrate (Fig. 2), possibly due to the hydrophobic interaction of cyclohexane with macromolecular chains of PVP ("hydrophobic pocket" in metal-enzymes).

It can be stated that the strength of polymer-carrier bond is determined by high donor capacity of nitrogen atom in polymer structure and by cooperative nature of polymer chain segments interaction with the carrier. Degree of acidity of the surface of carrier plays an important role in adsorption of PVP, since this polymer has a nitrogen-containing functional group capable of interacting with acid sites. According to traditional concepts, aluminosilicate has the greatest degree of acidity, and, therefore, a stronger bond PVP - adsorbent forms on this support. As is known, the concept of acid-base bond on the surface of mineral carriers is due to existence of Lewis and Brønsted acid-base centers. These centers serve to adsorb the molecules of various adsorbates. Irreversible adsorption of polymers takes place in the phase of inorganic carrier, which is very important for formation of strongly bonded polymer-metal complexes. In addition, Siral-40 has higher specific surface area (420 m<sup>2</sup>/g) in comparison with other carriers.

### Conclusions

New catalysts based on polymer-ferrocyanide complexes fixed on mineral supports have been developed for the process of cyclohexane oxidation with hydrogen peroxide. It was established that all prepared polymer-metal catalysts supported on inorganic substrates are active in cyclohexane oxidation.

Like biomimetic systems, these catalysts exhibit high activity and selectivity in cyclohexane oxidation under mild conditions. The nature of support affects activity and selectivity of synthesized catalysts. It was established that the acidic properties of the carriers' surface significantly affect selectivity of oxidation process.

The most selective for cyclohexanone is polyvinylpyrrolidone-ferrocyanide complex fixed on aluminosilicate with 40% of SiO<sub>2</sub> (conversion is 42.9%, cyclohexanone : cyclohexanol ratio is 5: 1).

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### ФЕРРОЦИАНИДТІ ПОЛИВИНИЛПИРРОЛИДОН-КАТАЛИЗАТОРЛАРЫНЫҢ ЦИКЛОГЕКСАНДА ТОТЫҒУЫ

**Аннотация.** Циклогександы тотықтыруға арналған катализаторлар дайындалды. Өртүрлі минералды полимерферроцианидті тасымалдағыштарға бекітілген катализаторлар адсорбциялық әдіспен дайындалды. Синтезделген катализаторлар циклогексанның сутегі қос тотығымен тотықтыру реакцияларында зерттелді. Тотықтыру жұмсақ жағдайда (шарттарда), яғни 40<sup>0</sup>С-ға және атмосферлік қысымда жүргізілді. Нәтижесінде барлық дайындалған полимерметалды катализаторлардың (бейорганикалық тасымалдағыштарда) циклогексанның тотығу процесінде белсенділігі артатыны анықталды.

Siral-40 тасымалдағышында дайындалған катализаторға қарағанда Siral-20 алюмосиликатында дайындалған полимерметалдық кешендердің белсенділігі 14%-ға жоғары 5%  $K_4[Fe(CN)_6]$ -ПВПД/Siral-40

катализаторының циклогексан бойынша селективтілігі айтарлықтай жоғары. Себебі 5%  $K_4[Fe(CN)_6]$ -ПВПД/Siral-20-да циклогексан бойынша селективтілік 61,7% тең болғанда сәйкесінше осы жағдайларда (Siral-40 катализаторында) селективтілік 83,4% құрайды.  $\gamma$ -  $Al_2O_3$ -ға дайындалған катализаторлардың белсенділігі алюмосиликаттарға (25,5%) қарағанда төмен (ОН:ОЛ=1,2:1). Осы уақытта 5%  $K_4[Fe(CN)_6]$ -ПВПД/ $SiO_2$

Катализаторында циклогексанның селективтілігі (70,4%) жоғары, конверсия 17,2% құрайды. Тасымалдағыш бетінің қышқылдық қасиетінің процесс селективтілігіне әсері зерттелді. Нәтижесінде тасымалдағыш табиғатының (бетінің қышқылдық қасиеті) синтезделген катализаторлар белсенділігі мен селективтілігіне айтарлықтай әсер ететіндігі анықталды.  $K_4[Fe(CN)_6]$ -ПВПД/Siral-40 поливинилпирролидон – ферроцианидті кешен өте жоғары каталитикалық қасиет көрсетеді. Циклогексанның конверсиясы 42,9%, ОН:ОЛ=5:1 арақатынасында циклогексанның селективтілігі 83,4% тең.

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