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 γ-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_2, 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^2/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_2 (conversion is 42.9%, cyclohexanone : cyclohexanol ratio is 5: 1).

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Л.К. Тастанова [1], А.К. Жармагамбетова [2],
Р.О. Орынбасар [1], А.К. Апендина [1], А.К. Жумабекова [3]

[1] Актюбинский региональный государственный университет им. К.Жубанова,
Актобе, пр. А. Молдагуловой, 34;
[2] Институт топлива, катализа и электрохимии им. Д.В. Сокольского, Алматы, ул. Кунаева, 142;
[3]Северо-Казахстанский Университет им. М. Козыбаева, Петропавловск, ул. Пушкина, 86

ФЕРРОЦИАНИДТІ ПОЛИВИНИЛПИРРОЛИДОН-КАТАЛИЗАТОРЛАРЫНЫҢ ЦИКЛОГЕКСАНДА ТОТЫҒУЫ

Аннотация. Циклогександы тотықтыруға арналған катализаторлар дайындалды. Әртүрлі минералды полимерферроцианидті тасымалдағыштарға бекітілген катализаторлар адсорбциялық әдіспен дайындалды. Синтезделген катализаторлар циклогексанның сутегі қос тотығымен тотықтыру реакцияларында зерттелді. Тотықтыру жұмсақ жағдайда (шарттарда), яғни 40^0С-та 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