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OXIDATION OF CYCLOHEXANE AND N-OCTANE TO KETONES AND ALCOHOLS UNDER MILD CONDITIONS

Abstract. PHMG-containing iron, chromium and manganese catalysts fixed on montmorillonite of the Taganskiy support (MMT) were synthesized for the liquid-phase oxidation of cyclohexane with hydrogen peroxide under mild conditions. The surface of the support was modified with water-soluble polymer - polyhexamethyleneurea (PHMG). Method of preparing the catalysts excludes step of reduction and calcination. By spectrophotometry the fixing of the active phase on the surface of the polymer-modified support was shown.

Previously, the process of hydrogen peroxide decomposition on the developed supported polymer-metal complexes was carried out. The synthesized catalysts showed activity in the decomposition reaction of H₂O₂ under mild conditions. Liquid-phase oxidation of cyclohexane and n-octane with hydrogen peroxide was carried out at a reaction temperature of 40°C and atmospheric pressure. Analysis data on the oxidation of hydrocarbons on the developed PHMG-modified bimetallic catalysts showed that the highest degree of hydrocarbon conversion observed on 10%Fe-Cr(1:1)-PHMG-MMT catalyst. By varying the nature of the solvent (acetonitrile + water and acetone + water), an increase in hydrocarbon conversion and selectivity of the process was achieved. When a water-acetone mixture is used as a solvent, the conversion of cyclohexane to cyclohexanol (COL) and cyclohexanone (CON) on 10%Fe-Cr(1:1)-PHMG-MMT reaches a maximum value and is 51.4%. The degree of n-octane conversion is 48.7%.

Key words: polymer-modified catalysts, hydrogen peroxide, oxidation, cyclohexane, montmorillonite.

Introduction
Oxidation reactions constitute an important group of processes in organic chemistry, but the toxicity of many commonly used oxidants and the need for the solvent are the main obstacles for further development of the technology [1-5]. One disadvantage of the process is the low selectivity. The search for new methods of oxidation in organic chemistry, and the use of "friendly" to the environment of solvents and oxidizing agents is relevant [6, 7]. In this regard, heterogenizing oxidation on catalysts with non-toxic hydrogen peroxide as the oxidant is a promising method of converting of hydrocarbons to a specific product [8-20].

The use of metal complexes immobilized on polymer-modified supports, as catalysts in oxidation of hydrocarbons is of great interest. The catalyst chemically tied with the support has improved stability and relieve the separation of the products after the reaction. The role of polymer is to stabilize the active phase.

In this regard, in the present work the catalytic properties of supports PHMG-modified catalysts of transition metals (iron, chromium and manganese) in the liquid-phase oxidation of cyclohexane and n-octane with hydrogen peroxide were studied.

The oxidation of cyclohexane with hydrogen peroxide conducted in a mixture of acetonitrile or acetone with water at a temperature of 40°C and atmospheric pressure.

The experimental part
Method of catalysts preparation based on the modification of the natural support (montmorillonite) the polymer with subsequent consolidation of the active phase. To obtain the active phase of the catalysts
were used salts of manganese (Mn(CH₃COO)₂·4H₂O), iron (FeCl₂), and chromium (KCrO₄). The polymer-modifier – polyhexamethylene guanidine (PHMG).

Catalysts were synthesized by the developed technique by mixing an aqueous solution of the polymer with the support, with the addition of aqueous solutions of metal salts. The resulting catalyst was dried at room temperature in air.

The concentration of metal ions in the catalyst was determined on spectrophotometer SF-2000 (Russia, 2015) from the calibration curve. Calibration was performed using a series of standard solutions of iron, chromium and manganese.

The activity of prepared catalysts in the decomposition of hydrogen peroxide was studied by the volumetric method at the rate of release of oxygen. A portion of the catalyst (0.03 g) in 5 ml of acetonitrile (acetone) and 5 ml of water were placed in a thermostated glass flask connected to a burette. In their experiments, the supply of H₂O₂ was carried out by a one-step introduction of the calculated amount of 0.9 ml of a 30% aqueous solution. The hydrogen peroxide concentration was determined with refractive index.

The oxidation reaction was carried out in a mixture of acetonitrile or acetone with water. In the catalystate obtained after decomposition of hydrogen peroxide, catalyst (0.03 g), a solution of water with acetonitrile or acetone in the ratio of 50:50, cyclohexane or n-octane (0.3 ml), 30% hydrogen peroxide (0.9 ml) were added to the initial reagents. The reaction temperature of 40 °C, pressure - atmospheric. The reaction duration 240 minutes for cyclohexane and 360 min for n-octane.

Analysis of the reaction products was performed on a chromatograph Khromos GC-1000 (“Khromos”, Russia) with a flame ionization detector in isothermal mode, using a capillary column BP21 (FFAP) with a polar phase (PEG modified nitroterephthalate) of length 50 m and internal diameter 0.32 mm. The column was maintained temperature of 40°C, the temperature in the evaporation chamber was 200°C, the support gas was the helium, the volume of injected sample 0.2 ml.

Results and discussion

10% bimetallic PGMG-modified Mn-Cr and Fe-Cr systems supported on montmorillonite (MMT) were synthesized.

The fullness of the deposition of the active phase on PGMG-modified support were recorded on a spectrophotometer SF-2000 at a calibration curve. It was shown the formation of the catalytic systems with the content of the active phase of ~ 10%.

Liquid-phase oxidation of cyclohexane and n-octane with hydrogen peroxide includes two parallel competing reactions – catalytic oxidation of activated hydrocarbons with oxygen with the formation of the desired products and the stoichiometric decomposition of H₂O₂ into water and inactive molecular oxygen which leaves the system in the form of gas.

The data of chromatographic analysis showed the formation in the case of cyclohexane – cyclohexanone and cyclohexanol, in the case of n-octane – ketones and alcohols.

The first stage the process of decomposition of hydrogen peroxide on the developed catalysts was carried out (figures 1 and 2).

It should be noted that the amount of oxygen released in the process of oxidation of cyclohexane on PHMG-modified catalysts is lower than in the decomposition of H₂O₂ (figures 1 and 2). This fact implies a process of oxidation of cyclohexane at atmospheric pressure on the developed catalysts.

When comparing the influence of the solvent response to the output products of the oxidation reaction it has been shown that the application of acetone as solvent increases the conversion of cyclohexane and n-octane more than 2 times. That is associated with the presence of acetic acid, acting as promoter of the reaction when carrying out the oxidation of acetone.

From the literature it is known that the presence in the solvent of acetic acid (which was discovered during studies of the oxidation process) contributes to the suppression of the competitive reaction of recombination of atomic oxygen in molecular, at the cost by increasing the rate of formation of oxidation products of cyclohexane.

The oxidation of cyclohexane optimal values of conversion obtained for 10% Fe-Cr(1:1)-PHMG-MMT catalyst and is 51.4%. The selectivity of the process by ketone ranges is 63.8%-88.6%.
Figure 1 - Number of released oxygen during the decomposition of hydrogen peroxide and in the oxidation of cyclohexane on synthesized catalysts in acetonitrile: 1 – 10% Fe-Cr(1:1)-PHMG/MMT; 2 – 10% Mn-Cr(1:1)-PHMG/MMT

Figure 2 - Number of released oxygen during the decomposition of hydrogen peroxide and in the oxidation of cyclohexane on synthesized catalysts in acetone: 1 – 10% Fe-Cr(1:1)-PHMG/MMT; 2 – 10% Mn-Cr(1:1)-PHMG/MMT

In the case of n-octane, has a smaller reactivity, were obtained lower values of conversion. The degree of conversion of hydrocarbons in aqueous-acetone medium is higher than in a solution of acetonitrile and reaches of 48.7% for 10% Mn-Cr(1:1)-PHMG-MMT.

Table 1 – Liquid-phase oxidation of cyclohexane on 10% synthesized bimetallic catalysts

<table>
<thead>
<tr>
<th>The catalysts</th>
<th>The reaction products, %</th>
<th>The conversion, %</th>
<th>S %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CON, %</td>
<td>COL, %</td>
<td></td>
</tr>
<tr>
<td>Water-acetonitrile medium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-Cr-PHMG-MMT</td>
<td>10,5</td>
<td>3,7</td>
<td>14,2</td>
</tr>
<tr>
<td>Fe-Cr-PHMG-MMT</td>
<td>25,2</td>
<td>14,3</td>
<td>39,5</td>
</tr>
<tr>
<td>Water-acetone medium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-Cr-PHMG-MMT</td>
<td>26,5</td>
<td>3,4</td>
<td>29,9</td>
</tr>
<tr>
<td>Fe-Cr-PHMG-MMT</td>
<td>38,3</td>
<td>13,1</td>
<td>51,4</td>
</tr>
</tbody>
</table>
It should be noted that the values for the conversion of n-octane on both catalysts have similar values. For the 10% Mn-Cr(1:1)-phmg-MMT catalyst – 48.7%, for 10% Fe-Cr(1:1)-phmg-MMT - 43.0%.

Table 2 - Liquid – phase oxidation of n-octane on the 10% synthesized bimetallic catalysts

<table>
<thead>
<tr>
<th>The catalysts</th>
<th>Продукты реакции, %</th>
<th>The conversion, %</th>
<th>S, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Σ ketones Σ alcohols</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetonitrile+water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1Mn-Cr-ΠГМГคร-MMT</td>
<td>23,3 3,1</td>
<td>26,4</td>
<td>S_{Σ ketones} -88,3</td>
</tr>
<tr>
<td>Fe-Cr-ΠГМГн-MMT</td>
<td>27,3 10,8</td>
<td>38,1</td>
<td>S_{Σ ketones} -71,7</td>
</tr>
<tr>
<td>Acetone + water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-Cr-ΠГМГн-MMT</td>
<td>12,9 35,8</td>
<td>48,7</td>
<td>S_{Σ alcohol} - 73,5</td>
</tr>
<tr>
<td>Fe-Cr-ΠГМГн-MMT</td>
<td>15,4 27,6</td>
<td>43,0</td>
<td>S_{Σ alcohol} - 64,1</td>
</tr>
</tbody>
</table>

The results obtained by the oxidation of cyclohexane and n-octane showed that the use of a mixture of acetone with water leads to increased conversion of substrates to oxygen-containing compounds. In the presence of the solvent the activity of PHMG-modified bimetallic catalysts increases.

Thus, a mixture of acetone with water is a promising solvent for the implementation of the oxidation of cyclohexane and n-octane with hydrogen peroxide under mild conditions, in the presence of which can be achieved with high values of conversion of the substrate.

Conclusions

Thus, supported on montmorillonite PHMG-modified catalysts of iron, chromium and manganese were synthesized with a content of active phase in the amount of 10%. The catalytic properties of PHMG-modified catalysts in the decomposition reactions of hydrogen peroxide and liquid-phase oxidation of cyclohexane and n-octane at 40°C and atmospheric pressure were studied.

It is shown that the developed catalytic systems are promising for the production of oxygenated compounds (alcohols and ketones).

By varying the nature of the solvent (acetonitril+water and acetone+water) improving the conversion of hydrocarbons and selectivity of the process was achieved. When used as solvent of water-acetone mixture, the highest conversion (51.4%) was obtained in the presence of PHMG-stabilized iron-chromium catalyst supported on montmorillonite. The degree of conversion of n-octane - 48.7%.

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REFERENCES

ЖУМСАҚ ЖАГДАЙДА ЦИКЛОГЕКСАН МЕН Н-ОКТАНДЫ КЕТОНДАР МЕН СПИРТЕРГЕ ДЕЙІН ТОТЫҚТЫРУ

Аннотация. Жұмсак жағдайдың сутек аскың тотығымен циклогексан мен н-октанды суық-фазалық тотықтыру ұрдасы үшін құрамаға темір, қром, марганец, ПГМГ бар Таган көрінісін алынған монтмориллонит тәсілі бекітілген каталитаторлар синтезделген. Тасымалдағыштың беттік кабытасы суда ерітін полимер полиэтиленсулфоаниддің (ПЭСА) мәдіниетінде. Катализаторлардың екінші қалыңғы құралдары болмайдығынан, ерідік пирофотометр метрліктері тасымалдағыштың мәдіниетінде бетқіл кабытасы болмайды және фазасын бекітіліктің рациады.

Алдың-ақа дайындалған бекітілген полимер-металды комплекстерге сутек аскың тотығымен құрылған ұрда құралған асқырларда. Синтезделген катализаторлар жұмсақ жағдайдын H2O2 жылық реакциясында білденділік керсете. Циклогексан мен н-октаның сутук аскың тотығымен суық-фазалық тотықтыру 40°C температура мен атмосфералық қысқамда жұрғізділ. Дайындалған ПГМГ-мәдіниетінде биометалды катализаторларға құмірсатын құралдардың бойынша алынған метрліктерін таңдау көмірсатын құрылымдардың әйелдең жоғары мәнін 10% Fe-Cr (1:1)-ПГМГ-ММТ катализаторында байқаладыымның көрсетілді.

Ерігінін табиғаты (ацетон+пентан+су) ерітінде көмірсатын құрылымдарға конверсиясы мен ұрдас селективтілігі жогарылық. Ерігінің ретінде сулы-ациетон косылған пайдалау кезінде циклогексаның конверсиясы 10% Fe-Cr (1:1)-ПГМГ-ММТ катализаторында максималды мәнге ерітінің 51,4% құрайды. Н-Октан әйелдең жөнінде – 48,7% құрайды.

Тірегі сөздер: полимер-мәдіниетіндегі катализаторлар, сутек аскың тотығы, тотықту, циклогексан, монтмориллонит.

УДК 542.943.7:546.215

ОКИСЛЕНИЕ ЦИКЛОГЕКСАНА И Н-ОКТАНА

Аннотация. Синтезированные ПГМГ-содержащие катализаторы, обеспечивая хрома и марганца, нанесенные на монтмориллонит Таганского месторождения (ММТ), для процесса жидкого окисления циклогексана и н-октана проксессом водорода в мягких условиях. Поверхность носителя модифицировали водорасторопным полимером – полиэтиленсулфоанидном (ПЭСА). Методика приготовления катализаторов
исключает стадии восстановления и прокаливания. Данные спектрофотометрии подтвердили закрепление активной фазы на поверхности модифицированного полимером носителя.

Предварительно осуществлялся процесс разложения пероксида водорода на разработанных нанесенных полимер-металлических комплексах. Синтезированные катализаторы проявили активность в реакции разложения H₂O₂ в мягких условиях. Жидкофазное окисление циклогексана и n-октана пероксидом водорода проводили при температуре реакции 40°С и атмосферном давлении. Анализ данных по окислению углеводородов на разработанных ПГМГ-модифицированных биметаллических катализаторах показал, что наибольшая степень превращения углеводородов наблюдается на 10%Fe-Cr(1:1)-ПГМГ-ММТ катализаторе.

При варьировании природы растворителя (ациетонил+вода и ацетон+вода) было достигнуто повышение конверсии углеводородов и селективности процесса. При использовании в качестве растворителя водно-ациетоновой смеси конверсия циклогексана в циклогексанол (ЦОЛ) и циклогексанон (ЦОН) на 10%Fe-Cr(1:1)-ПГМГ-ММТ достигает максимального значения и составляет 51,4%. Степень превращения n-октана - 48,7%.

**Ключевые слова:** полимер-модифицированные катализаторы, пероксид водорода, окисление, циклогексан, монтмориллонит.

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