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## OXIDATION OF CYCLOHEXANE ON COPPER AND COBALT CATALYSTS SUPPORTED ON PECTIN-MODIFIED OXIDES AND TAGANSKY MONTMORILLONITE

**Abstract.** Supported copper and cobalt catalysts based on pectin (PC) have been synthesized for the process of cyclohexane oxidation with hydrogen peroxide under mild conditions. Synthetic oxides (MgO, Al<sub>2</sub>O<sub>3</sub>, ZnO) and natural montmorillonite of the Tagansky deposit (TS) were used as supports. Cyclohexane oxidation was carried out in acetonitrile at 40°C and atmospheric pressure in a thermostated reactor with constant stirring. The most effective were copper catalysts. The optimal support for fixing the active phase (Cu<sup>2+</sup>) was found the montmorillonite of the Tagansky deposit. Among the copper catalysts, the most active was a pectin-containing catalyst supported on TS, on which the conversion of cyclohexane was 11.2%.

**Key words:** Cyclohexane, oxidation, montmorillonite, pectin, copper catalysts, cobalt catalysts.

Clays are widespread, easily available and low-cost chemicals. Both in their native state and in numerous modified forms, clays are versatile materials. In recent years, clays are attracted chemist attention as a potential supports for heterogeneous catalysts due to their abundance, inertness, ability for simple methods of modification of textural properties. Clays structure can be varied by different methods to suit requirements for specific catalytic targets. The textural properties may be improved by intercalation. The formation such materials increases the thermal stability of the obtained material with respect to the natural clay and also generates microporosity in the final material [1]. Clays can be intercalated with a variety of inorganic and organic ions, metal complexes, and organic compounds. Polymer-clay composites at present time are consider as promising materials for both industrial and fundamental purposes [2]. Among them, a montmorillonite is one of the most intensively explored catalytic materials in heterogeneous catalysis due to its low cost and eco-friendliness [3]. The montmorillonite of Tagansky deposit (TS) is a promising material for development new types of catalysts supported on polymer-clay matrix. The use of renewable plant polymers as polysaccharides for the synthesis of such composites and their application in the catalysis meets the requirements of the twelve principles of green chemistry.

The partial catalytic oxidation of paraffins is of particular interest to industry, as it allows the production of valuable oxygen-containing products from crude hydrocarbons. The proper developed catalysts is critical to produce target products based on these processes. A promising approach is to create heterogeneous polymer-metal catalysts that demonstrate significant activity and selectivity in various oxidation reactions at low temperatures and pressures.

In this work, we present the results of a study of the catalytic activity of supported copper and cobalt catalysts in cyclohexane oxidation with hydrogen peroxide under mild conditions. Synthetic oxides

(MgO, Al<sub>2</sub>O<sub>3</sub>, ZnO) and natural montmorillonite (TS) were used as supports. Pectin (PC), obtained from sugar beet pulp, was applied to produce polymer-modified supports. The catalysts were prepared by the previously developed method of consequent adsorption of polymer and then metal salts on support [4]. According to transmission electron microscopy data, the introduction of pectin into the supported catalysts promotes the formation of metal (Cu or Co) nanoparticle on the surface of the support [5]. The metal content in the catalyst was 1wt. %.

Cyclohexane oxidation was carried out in acetonitrile, as solvent, at 40°C and atmospheric pressure in a thermostated reactor with constant stirring. The reaction time was 4 hours. Hydrogen peroxide was used as oxidising agent. In the first runs, the catalysts tested in hydrogen peroxide decomposition under mild conditions. The activity of the copper catalysts in this reaction decreased, depending on the nature of the supports, as follows: Cu-PC/ZnO > Cu-PC/Al<sub>2</sub>O<sub>3</sub> > Cu-PC/ TS > 1% Cu-PC/MgO. The rate of O<sub>2</sub> evolution on pectin-containing cobalt catalysts decreased in the following sequence: Co-PC/Al<sub>2</sub>O<sub>3</sub> > > Co-PC/TS > Co-PC/ZnO > Co-PC/MgO.

Oxidation of cyclohexane with hydrogen peroxide is accompanied with lower volume of oxygen release. This indicates participation of the oxygen in the cyclohexane oxidation. Chromatographic analysis detected formation only two products: cyclohexanone (C-none) and cyclohexanol (C-ol), which are call as KA-oil (ketone and alcohol). It should be noted that more amount of ketone to compare with alcohol was formed on all of the catalysts studied. The C-none:C-ol ratio, depending on the nature of the catalyst, ranged from 1.1 to 1.6 (table). Among the copper catalysts, the most active was a pectin-containing catalyst supported on TS, on which the conversion of cyclohexane was 11.2% (table). The yield of KA-oil decreased on the following row: TS > Al<sub>2</sub>O<sub>3</sub> > MgO > ZnO.

In the case of cobalt catalysts, the highest conversion was achieved on 1%Co-PC/Al<sub>2</sub>O<sub>3</sub> (5.8%). The following regularity was found. The activity of catalysts characterized by an acidic properties and a high specific surface area of supports (TS = 100.7 m<sup>2</sup>/g and alumina = 96.0 m<sup>2</sup>/g) was higher than on basic oxides (ZnO = 7.5 m<sup>2</sup>/g and MgO = 6.8 m<sup>2</sup>/g) [6].

Oxidation of cyclohexane on 1% pectin-containing copper, cobalt catalysts deposited on the various supports

| Catalyst                             | Reaction products |                 | Conversion, % | Ratio of C-none: C-ol |
|--------------------------------------|-------------------|-----------------|---------------|-----------------------|
|                                      | Cyclohexanone, %  | Cyclohexanol, % |               |                       |
| Cu-PC/TS                             | 6.4               | 4.8             | 11.2          | 1.3                   |
| Cu-PC/Al <sub>2</sub> O <sub>3</sub> | 5.9               | 4.0             | 9.9           | 1.5                   |
| Cu-PC/ZnO                            | 3.0               | 2.0             | 5.0           | 1.5                   |
| Cu-PC/MgO                            | 2.5               | 1.7             | 4.2           | 1.1                   |
| Co-PC/TS                             | 2.9               | 1.8             | 4.7           | 1.6                   |
| Co-PC/Al <sub>2</sub> O <sub>3</sub> | 3.3               | 2.5             | 5.8           | 1.3                   |
| Co-PC/ZnO                            | 2.4               | 1.7             | 4.1           | ~1.4                  |
| Co-PC/MgO                            | –                 | –               | –             | –                     |

Thus, the copper and cobalt catalysts based on pectin-modified oxides and TS were synthesized and studied in the reactions of decomposition of hydrogen peroxide and oxidation of cyclohexane. The most effective were copper catalysts. The optimal support for fixing the active phase (Cu<sup>2+</sup>) was found the monmorillonite of the Tagansky deposit.

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### ПЕКТИН-МОДИФИЦИРЛЕНГЕН ОКСИДТЕРГЕ ЖӘНЕ «ТАҒАН» КЕН ОРНЫНЫҢ МОНТМОРИЛЛОНИТІНЕ БЕКІТІЛГЕН МЫС ЖӘНЕ КОБАЛЫТ КАТАЛИЗАТОРЛАРДЫҢ ҚАТЫСУЫ АРҚЫЛЫ ЦИКЛОГЕКСАНДЫ ТОТЫҚТЫРУ

**Аннотация.** Жұмсартылған жағдайда сутегі асқын тотығымен циклогександы тотығу үдерісі үшін пектин (ПК) негізінде мыс және кобальтты катализаторлар синтезделді. Тасымалдағыштар ретінде синтетикалық оксидтер (MgO, Al<sub>2</sub>O<sub>3</sub>, ZnO) және табиғи Таған кен орнының монтмориллониті (ТС) пайдаланылды. Циклогексанның тотығуы ацетонитрилде 40°C температурада, атмосфералық қысымда және термостатирленген реакторда тұрақты араластыру арқылы жүргізілді. Мыс катализаторларының тиімділігі анықталды. Белсенді фазаны (Cu<sup>2+</sup>) бекіту үшін оңтайлы тасымалдаушы Таған кен орнының монтмориллониті табылды. Мыс катализаторларының арасында ТС негізіндегі құрамында пектин кездесетін катализатордың белсенді екені анықталды, ондағы циклогексан конверсиясы 11,2% құрады.

**Түйін сөздер:** Циклогексан, тотығу, монтмориллонит, пектин, мыс катализаторлары, кобальтті катализаторлар.

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### ОКИСЛЕНИЕ ЦИКЛОГЕКСАНА НА МЕДНЫХ И КОБАЛЬТОВЫХ КАТАЛИЗАТОРАХ, НАНЕСЕННЫХ НА ПЕКТИН-МОДИФИЦИРОВАННЫЕ ОКСИДЫ И МОНТМОРИЛЛОНИТ ТАГАНСКОГО МЕСТОРОЖДЕНИЯ

**Аннотация.** Были синтезированы нанесенные медные и кобальтовые катализаторы на основе пектина (ПК) для процесса окисления циклогексана пероксидом водорода в мягких условиях. В качестве носителей были использованы синтетические оксиды (MgO, Al<sub>2</sub>O<sub>3</sub>, ZnO) и природный монтмориллонит Таганского месторождения (ТС). Окисление циклогексана проводили в ацетонитриле при температуре 40°C и атмосферном давлении в термостатированном реакторе с постоянным перемешиванием. Наиболее эффективными оказались медные катализаторы. Оптимальным носителем для фиксации активной фазы (Cu<sup>2+</sup>) является монтмориллонит Таганского месторождения. Среди медных катализаторов наиболее активным является пектинодержательный катализатор на основе ТС, на котором конверсия циклогексана составила 11,2%.

**Ключевые слова:** циклогексан, окисление, монтмориллонит, пектин, медные катализаторы, кобальтовые катализаторы.

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## REFERENCES

[1] Dasgupta S., Török B. (2008) Application of clay catalysts in organic synthesis. A review, *Organic Preparations and Procedures International*, 40(1): 1-65. DOI: 10.1080/00304940809356640 (in Eng.).

[2] Kausar A. (2017) Physical properties of hybrid polymer/clay composites, *Hybrid Polymer Composite Materials*, 115-132. DOI:10.1016/b978-0-08-100787-7.00005-6 (in Eng.).

[3] Luna F., Cecilia J., Saboya R., Barrera D., Sapag K., Rodríguez-Castellón E., Cavalcante C. (2018) Natural and Modified Montmorillonite Clays as Catalysts for Synthesis of Biolubricants, *Materials*, 11(9): 1764. DOI: 10.3390/ma11091764 (in Eng.).

[4] Zharmagambetova A.K., Zhurinov M. (2019) Polysaccharide-stabilized palladium nanocatalyst for semi-hydrogenation of complex alkynols // *News of the Academy of sciences of the Republic of Kazakhstan. Series chemistry and technology*, 5: 143-149. DOI: 10.32014/2019.2518-1491.66 (in Eng.).

[5] Zharmagambetova A.K., Seitkalieva K.S., Talgatov E.T., Auezkhanova A.S., Dzhardimalieva G.I., Pomogailo A.D. (2016) Polymer-modified supported palladium catalysts for the hydrogenation of acetylene compounds, *Kinetics and Catalysis*, 57: 360-367. DOI: 10.7868/S0453881116030175 (in Eng.).

[6] Zharmagambetova A.K., Selenova B.S., Safarov R.Z., Shapovalov A.A. (2006) The effect of surface acid-base characteristics of some supports on the catalytic properties of the Mn (II) polymer-ferrocyanide complex // *News of the Academy of sciences of the Republic of Kazakhstan. Series of chemistry [Izvestiya nacionalnoj akademii nauk Respubliki Kazahstan. Seriya himicheskaya]*, 4: 21-24 (in Russ.).