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HYDROGENATION OF BENZENE IN BATCH REACTOR

Abstract. In this article is considered hydrogenation of benzene in liquid phase at presence rhodium support catalyst where as carrier is used pillar structural montmorillonite obtaining from bentonite clay. The degree of using an internal surface of porous system is depended of the size particles. Increase the concentration of chromium above 20 mmole per gram of clay does not lead to the further growth of distance. It is probably connected by that in a solution there are not hydrolyzed forms of chromium chloride which do not influence formation pillar structures. Modifying montmorillonite minerals containing in bentonite clay gives to them heat resistance. The specific surface of samples (containing 15-30 mmole Cr³⁺) were defined after heat treatment at 180°C are 240-260 m²/g and increasing the temperature up to 500-560°C decreases this value insignificant to 220-240 m²/g, accordingly. Not modified bentonite clay lost their porosity at 140°C, and a specific surface made 20 m²/g.

Besides reaction of hydro-dehydrogenation of cyclic hydrocarbons a huge interest are represented in hydrogen technology. Everyone mole of benzene and its derivatives attaching of three and more quantities of hydrogen, and are unique objects at storages and transportation of hydrogen. Thereby, necessity to develop of catalysts of hydro-dehydrogenation also follows under rather soft conditions. developed rhodium support catalyst for hydrogenation of benzene and defined the factor of efficiency using the internal surface of porosity systems. Presence of water in hydrogenated system leads to phasic course of restoration of benzene on a surface of the catalyst with formation cyclohexane and cyclohexene. The received experimental results expand a circle of data in the field of hydro-dearomatization motor fuels, especially transformations of aromatic hydrocarbons cycloalkans.

Keywords: hydrogenation, benzene, liquid phase, rhodium, catalyst, cycloalkane.

Introduction. Decrease in the maintenance of aromatic hydrocarbons, especially benzene in motor fuel is an actual and urgent problem. Toxic action of benzene and a product of its incomplete oxidation benzopyrene - cancerogenic substance accumulated in an environment, renders negative influence on safety of ability to live of people and fauna [1]. Necessity to improve technology of oil refining and its separate stages for reduction of the maintenance of benzene and its

derivatives. One of such processes is catalytic hydrodearomatization-transformations of aromatic hydrocarbons to cyclohexane and its derivatives. However, the maintenance in oil distillates heterocyclic compounds which deactivate catalysts, demand their perfection and more detailed studying of the mechanism catalytic transformation of hydrocarbons [2-8].

Besides reaction of hydro-dehydrogenation of cyclic hydrocarbons a huge interest are represented in hydrogen technology. Every one mole of benzene and its derivatives attaching of three and more quantities of hydrogen, and are unique objects at storages and transportation of hydrogen. Thereby, necessity to develop of catalysts of hydro-dehydrogenation also follows under rather soft conditions.

The aim of the present work was studying the hydrodearomatization of benzene—the component of motor fuels at presence rhodium support catalysts where as carrier is used pillar structural montmorillonite obtaining from bentonite clay. Pillared clays have significant potential for application in industry and in petrochemistry but relatively few studies of these types of materials have been carried out [9].

EXPERIMENTAL PART

Catalysts and their preparations. For preparation rhodium support catalyst (0,5-1,0 mass. % Rh) was used chloride of rhodium- $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, as a carrier was used modified bentonite clay. For modifying natural clay to pillar structural form were used polyhydroxocomplexes of chromium [5].

To aqueous solution of chloride chromium gradually flowed the solution of sodium hydroxide at gradual hashing up to pH~3-4. Concentration of chloride chromium was paid off proceeding from calculation 5-30 mmole Cr^{3+} per gram clay. Suspension bentonite (~1,0 mass. %) received by intensive hashing it in water during 4 h, pH-water extract of clay makes -8-9. Acidity of environment supervised by means of digital pH meter OP-208/1. In order to prevent coagulation of a solution polyhydroxocomplexes of chromium, it was slowly added to suspension of clay. «Reserve of basicity» $\text{Cr}^{3+}/\text{OH}^-$ —allowing to prevent coagulation chloride of rhodium made 1/3. After endurance processed suspensions of clay during 24 h, a deposit was washed by water and condensed. The sample, after separate from a liquid phase, dried at first at the room temperature, and then at 110°C (2h) with the subsequent rise the temperature up to 180°C (4h). After cooling the firm mass was pounded to a powder, it was sifted in fractions with the certain sizes of particles. Fractions of particles modifying clay in the further was impregnated with aqueous solution of rhodium- $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0,5-1,0 mass% Rh). The received dense mass was dried on a water bath, then subjected heat treatment during 6 h at 180°C.

Definition of catalytic activity. Before experience sample of the catalyst 0,1g was reduced by hydrogen at 250 °C during 4 h. After reduction the catalyst was cooled in the environment of hydrogen up to a room temperature and under a layer of cyclohexane was transferred to a steel autoclave with working capacity 100 cm³ the supplied by mixer and a sampler. For the hydrodearomatization is taken 50 cm³

mixture of benzene and cyclohexane/V (benzene:V(cyclohexane) = 1:1/ Dilution by cyclohexane was made for dispersion of heat allocated athydrogenation of benzene and aspiration process to spend in conditions of ideal mixture. Initial rate of hydrogenation was defined by differential graphic method from the change concentration of benzene independence of time. Pressure of hydrogen was measured by a manometer and varied in an interval 0.5-6.0 МПа, and temperature of reactions changed from 120 up to 200 °C.

X-raying analyse of samples was obtained on diffractometer using CuK - radiation. A specific surface of catalysts it was defined by adsorption method.

The analysis of reaction products were spent by Chrom-4. Length of a column is 3 m, diameter - 3 mm filled by firm carrier « Chromaton-N» processed with liquid phase « Polyethylenglycol adipate» (15 % mass. of the carrier).

Temperature of a column 100°C, temperature of the evaporator 150 °C. Gas carrier-argon, velocity of the gas ocarrier - 50 cm³/minute. 0,50-0,54 cm³/g, interlaminar distances d₀₀₁ from 0,90 up to 2,04 nanometers.

RESULTS AND DISCUSSION

Using adsorbents of pillar structural form in catalyse and sorbtion processes was an incitement for development of methods of their synthesis and their reception from natural clay. Table 1 shows some physical characteristics of rhodium support-catalyst where as carrier is served pillar structural montmorillonite containing in bentonite clay received from the South-Kazakhstan area of Republic Kazakhstan. Modifying bentonite clay by polyhydroxocomplexes Cr(III) leads to growth of a specific surface from 64 up to 260 m²/g, total volume of porous from 0,18 cm³/g up to 54 cm³/g, interlaminar distances from 0.90 up to 2.04 nm.

Table 1 – Some parameters of pillar structural montmorillonite modified by chromium

The maintenance of ions chromium, mmole/g. clay	S, m ² /g	d ₀₀₁ nano meter	Total volume of porous, cm ³ /g	Loss of thermostability	
				T, °C	S _{SP} , m ² /g
–	64	0,90	0,18	140	20
5	130	1,30	0,40	360	80
10	160	1,60	0,46	440	110
15	240	2,02	0,50	500	220
20	260	2,04	0,54	560	240
30	240	1,90	0,51	500	230

The maximal distance 2,00-2,04 nanometers corresponds to concentration of chromium about 15-20 mmole per gram of clay where between the layers settle down polyhydroxocomplexions of chromium [6].

Increase the concentration of chromium above 20 mmole per gram of clay does not lead to the further growth of distance. It is probably connected by that in a

solution there are not hydrolized forms of chromium chloride which do not influence formation pillar structures. The similar phenomenon with polyhydroxocomplex ions of iron (III) also was revealed in [7]. Modifying montmorillonite minerals containing in bentonite clay gives to them heat resistance. The specific surface of samples (containing 15-30 mmole Cr^{3+}) were defined after heat treatment at 180°C are $240\text{-}260 \text{ m}^2/\text{g}$ and increasing the temperature up to $500\text{-}560^\circ\text{C}$ decreases this value insignificant to $220\text{-}240 \text{ m}^2/\text{g}$, accordingly. Not modified bentonite clay lost their porosity at 140°C , and a specific surface made $20 \text{ m}^2/\text{g}$.

Received modified montmorillonite was used for preparation rhodium support catalysts (0,5-1,0 mass. % Rh) which was used for hydrogenation of benzene.

The specific surface of support catalysts are enough and firstly were defined influence of an internal surface of catalysts to the hydrogenation rate of benzene. In order to was defined a criterion Tyle -Zeldovich which directly proportional to the resulted radius of the catalyst

$$\phi = R_0 \sqrt{\frac{k}{D}},$$

where R_0 – the resulted radius of particles of the catalyst (for spherical particle $R_0=R/3$); k – a constant of rate of reaction; D – effective factor of diffusion of reacting molecules on a surface inside of porous

For gases the factor of diffusion has the order of $0,1 \text{ cm}^2/\text{sec}$, and for liquid molecular diffusion $\sim 10^{-5} \text{ cm}^2/\text{sec}$. [8]. On their data, the factor of diffusion for gas dissolved in a liquid has the same order, as for the liquid of $10^{-5} \text{ cm}^2/\text{sec}$. At 120°C saturated vapor pressure of benzene, is equal 2 bar. Fugacity of benzene vapor in this condition is equal $f \sim 0,80$ bar. Activity coefficient of liquid benzene at 120°C and 40 bar is equal 0.95. At the general of pressure of system 40 bar fugacity of benzene is equal to 38 bar. Constant of phase balance: $k=47.5$ which allows to judge that benzene is basically in a liquid phase Constant reaction rate of hydrogenation of benzene was defined at presence of a powder of the catalyst with the average size of particles about 0,1 mm which has value $2,3 \cdot 10^{-2} \text{ sec}^{-1}$. The factor of efficiency - a degree of use of an internal surface is defined from the relation $\frac{\text{th}\phi}{\phi}$, and the value of $\text{th}\phi$ calculated by equality:

$$\text{th}\phi = \frac{[\exp(\phi) - \exp(-\phi)]}{[\exp(\phi) + \exp(-\phi)]}.$$

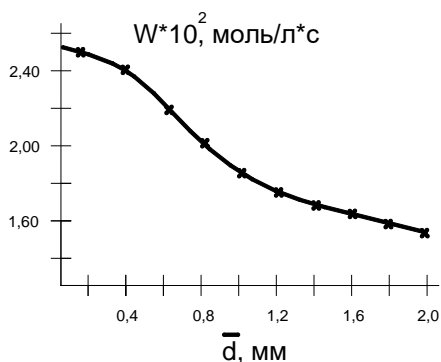
The calculated values of parameters for hydrogenation of benzene at presence of porous catalysts are shown in table 2.

Data of table 2 shows, that using the catalysts with average diameter of articles about 1 mm the factor of efficiency is 0.86 and at 2 mm - 0,63. On the basis of these data, it is possible to conclude that the internal surface of system is used effectively, at the size of particles of catalysts less than 0.8 mm.

For the subsequent experiences at the hydrogenation of benzene were used catalysts with the average size of particles less than 0,4 mm. As experiences were spent at intensive hashing (2000 rev/min) the influence of external diffusion can be neglected.

Table 2 – Change the factor of efficiency from the size of particles on the 0,5 % Rh/carrier
 Condition: m (kt) = 0,1 g, t = 120°C, P (H₂) = 40 bar., C(benzene) = 2.8 mol/L

The average size of diameter of particles of the catalyst, mm	φ	th φ	η
0,2	0,13	0,14	0,99
0,4	0,31	0,30	0,98
0,6	0,47	0,44	0,94
0,8	0,62	0,55	0,90
1,0	0,75	0,64	0,86
2,0	1,56	0,97	0,63



Condition: t = 120 °C; P(H₂) = 40 bar. C(benzene) = 2.8 mol/L

Figure 1 – Change of rate hydrodearomatization as a function of the size catalyst particles

At the hydrogenation of benzene, in the studied conditions, the unique product of reduction was cyclohexane.

The change acidity of support catalysts often leads to change its selectivity.

Well-known, preadsorbed water promotes formation variety acid and basicity centers of surface [3].

Next experimentation carry on to figure out the influence of water to hydrogenation of benzene at presencesupport catalysts where as carrier is used pillar structural montmorillonite modifyingby polyhydroxocomplex chromium. Results of hydrogenation of an aromatic ring are presented in table 3.

From table 3 follows, presence of water in system at hydrogenation of benzene on 20 minute of process leads to formation of 6 % mass cyclohexeneand 28 % mass.of cyclohexane . The further increase in volume of water leads to reduction of an output of products of hydrogenation.

In our opinion, the aromatic ring, after connection of four atoms of hydrogen is hydrogenated up to cyclohexane not leaving a surface of the catalyst. Alongside with it, it is possible to believe, formed cyclohexeneis superseded by molecules of water [10-12].

Table 3 – Hydrogenation of benzene at presence of water on 0,5 % the Rh/carrier.
Condition: m (kt) = 0,1 r, t = 120°C, P (H₂) = 40 atm.

Initial mix, ml			Output of products of hydrogenation (% mass.) on time, minute					
			C ₆ H ₁₀	C ₆ H ₁₂	C ₆ H ₁₀	C ₆ H ₁₂	C ₆ H ₁₀	C ₆ H ₁₂
C ₆ H ₆	C ₆ H ₁₄	H ₂ O	10		20		30	
25	25	–	–	30	–	58	–	74
25	20	5	2,5	20	4,0	36	3,0	48
25	15	10	3,0	18	6,0	28	5,0	41
25	10	15	2,0	14	3,0	24	3,0	30
25	5	20	1,0	10,0	2,0	14	2,0	18

The given circumstance testifies in favour of consecutive connection of hydrogen to aromatic ring.

However, in reactionary system the formation of cyclohexadiene which should be superseded also by molecules of water from the surface of catalyst is not observed. Probably, velocity of hydrogenation of cyclohexadiene prevails its desorption. Alongside with it it is possible to believe, that formation intermediate cycloolefines promotes character of adsorption of benzene which can be carried out in the form of plane and costal orientation. Combinations of the support rhodium catalyst at presence of molecules of water creates favorable conditions to destruction - electronic system of an aromatic ring, focusing costal adsorption of benzene. Probably, in structure of the activated complex benzene participates with 4p-electrons of rings which subsequently attaches four atoms of hydrogen. The given assumption does not contradict 18-electronic rule [13].

Conclusion. Thus, it is developed rhodium supportcatalyst forhydrogenation of benzene and defined the factor of efficiency using the internal surface of porosity systems. Presence of water in hydrogenated system leads to phasic course of restoration of benzene on a surface of the catalyst with formation cyclohexane and cyclohexene. The received experimental results expand a circle of data in the field of hydrodearomatization motor fuels, especially transformations of aromatic hydrocarbons cycloalkans.

REFERENCES

- [1] Magaril R.E., Magaril R.Z. Motor Fuels. M.: KDU, 2008. 159 p.
- [2] Elfghi F.M. Amin NAS. Influence of tin content on the texture properties and catalytic performance of bi-metallic Pt–Re and tri-metallic Pt–Re–Sn catalyst for n-octane reforming // Reaction Kinetics, Mechanisms and Catalysis. 2015. No. 114 (1). P. 229-249.
- [3] Krylov O.V. Heterogeneous catalysis. M.: IKS Academbook, 2004. 679 p.
- [4] Nefedov B.K. // Catalysis in industry. 2001. No. 1. P. 48.
- [5] Nagy G., Varga Z., Kallo D., Hancsok J.. Investigation of hydrogenation of aromatic hydrocarbons on Pt/Pd/USY catalyst // Hungarian journal of Industrial chemistry. 2009. Vol. 37(2). P. 69-75.

- [6] Rozengart M.I., V'yunova G.M., Isagulyants G.V. Layered Silicates as Catalysts // Russ. Chem. Rev. 1988. Vol. 57, No. 2. P. 115-128. DOI: <https://doi.org/10.1070/RC1988v057n02ABEH003339>
- [7] Komarov V.S., Panasjugin A.S., Trofimenko N.E. // Colloid Journal. 1975. Vol. 37, N 1. P. 51-56 (in Russ.).
- [8] Magaril R.Z. Theoretical of a basis of chemical processes oil refining. M.: Chemistry, 1976. 312 p.
- [9] Utelbayeva A.B., Utelbayev B. T., Ermachanov M. Hydrogenation of benzene in the presence of ruthenium deposited on modified montmorillonite // J. Phys. chemical. 2013. Vol. 87, No. 9. P. 1486-1489.
- [10] Zhanabaev B.Z., Zanozina P.P., Utelbayev B.T. Selective Hydrogenation of Benzene over Ruthenium catalyst // Kinetics and Catalysis. 1991. Vol. 32. P. 214-218.
- [11] Don G.A., Scholten G.G. // J. Chem. Soc. Faraday Trans. II. 1981. Vol. 72. P. 145.
- [12] Rozovskii A.Ya., Vytнова L.A., Tret'yakov V.F., Lin G.I., Yanyukova A.M. // Kinetics and Catalysis. 1982. Vol. 23, No. 6. P. 1401.
- [13] Tolman C.A. The 16 and 18 electron rule in organometallic chemistry and homogeneous catalysis // Chem. Soc. Rev. 1972. Vol. 1. P. 337-353. <https://doi.org/10.1039/CS9720100337>
- [14] The General organic chemistry. M.: Chemistry, 1984. Vol. 7. 472 p.

Резюме

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ПЕРИОДТЫ РЕАКТОРДА БЕНЗОЛДЫ ГИДРОГЕНИЗАЦИЯЛАУ

Келтірілген статъяда тасымалдағышқа отырғызылған родий катализаторы қатысында сұйық фазада бензолды гидрогенизациялау қақарастырылған. Тасымалдағыш ретінде бентонит сазын құрайтын монтмориллонит минералы пайдалынады, Бентонит сазына кеуекті құрылым беру үшін полигидроксиокомплекс түзетін хром ионары пайдаланылған. Кеуекті құрылым алу барысында әрбір грамм топырақ сазына 20 ммоль хром ионының мөлшері жеткілікті. Концентрацияны арттыру барысында хромның гидролизге ұшырайтындығы ескерілген. Монтмориллонитке берілген кеуекті құрылым тасымалдағыш бойына термиялық тұрақтылық және оның меншікті аудан бетінің артуына себепші болады. Құрамында 15-30 ммоль Cr^{3+} мөлшері бар кеуекті құрылымды бентонитті 180 °С температурасында қыздыруға ұшыратып өңдегеннен соң оның меншікті аудан беті 240-260 м²/г, шамасын, ал температураны 500-560 °С дейін жоғарылатқанда, шамала ғана 220-240 м²/г, шамасына өзгертіндігі анықталған. Өңделмеген бентонит саз топырақтары кеуектіліктерін 140°С температурасында қыздырғанда жоғалтады және бұл 20 м²/г шамасында болады. Кеуекті құрылымның ішкі қуыс беттерін пайдалану, алынған бөлшектердің өлшем түріне байланысты болады. Аталынған гидрлеу – дегидрлеу реакциялары газ күйіндегі сутекті тасымалдау және сақтау мәселелерімен айналысатын сутектік технология саласын да қатты қызықтыруда. Ароматты сақинаның әрбір молі өзінен үш есе көп мөлшердегі сутегіні құрамына қосып алады. Демек, тиімді технологиялық жағдайларда гидрлеу үдерісін жүзеге асыру үшін химиялық өзгерістерді оңтайлы жүргізетін катализаторлар жүйелерін алу және оларды синтездеу мәселелері туын-

дайды. Аталған мәселелерді шешу жолында тасымалдағыш бетіне отырғызылған родий қосылыстары қарастырылды. Алынған катализаторлардың ішкі қуыс беттерін пайдалануды сипаттайтын коэффициент шамасы анықталынды. Үдерісті жүргізу барысында әрекеттесу жүйесінде аздаған су болуы химиялық реакцияның циклогексен арқылы сатылап өтетіндігін көрсетеді. Алынған мәліметтер ароматикалық сақиналы қосылыстарды сутекпен катализатор қатысында циклоалкандарға айналдыру тұрғысындағы мәліметтерді кеңейтеді.

Түйін сөздер: гидрлеу, бензол, сұйық фаза, реактор, родий, катализатор, циклоалкан.

Резюме

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ГИДРОГЕНАЦИЯ БЕНЗОЛА В РЕАКТОРЕ ПЕРИОДИЧЕСКОГО ДЕЙСТВИЯ

В статье рассматривается гидрирование бензола в жидкой фазе в присутствии нанесенного родиевого катализатора. В качестве носителя используется столбчатый структурный монтмориллонит, получаемый из бентонитовой глины. Повышение концентрации хрома выше 20 ммоль на грамм глины не приводит к дальнейшему росту расстояния. Вероятно, это связано с тем, что в растворе отсутствуют гидролизированные формы хлорида хрома, которые не влияют на формирование столбчатых структур. Модификация минералов монтмориллонита, содержащихся в бентонитовой глине, придает им термостойкость. Удельная поверхность образцов (содержащих 15-30 ммоль Cr^{3+}), определенная после термообработки при 180 °С, составляет 240-260 м²/г, а повышение температуры до 500-560 °С снижает это значение значительно до 220-240 м²/г, соответственно. Немодифицированная бентонитовая глина потеряла пористость при 140 °С, а удельная поверхность составила 20 м²/г. Степень использования внутренней поверхности пористой системы зависит от размера частиц. Реакции гидрирования – дегидрирования циклических углеводородов огромный интерес представляют в водородной технологии для сохранения газообразного водорода. Каждый моль бензола и его производные присоединяют три и более количества водорода, и является уникальным объектом при хранении и транспортировке газообразного водорода. Таким образом, необходимость разработки катализаторов гидродегидрирования также возникает в достаточно мягких условиях. Разработан родиевый носитель катализатора для гидрирования бензола и определен коэффициент полезного действия с использованием внутренней поверхности пористых систем. Присутствие воды в гидрогенизированной системе приводит к поэтапному процессу восстановления бензола на поверхности катализатора с образованием циклогексана и циклогексена. Полученные экспериментальные результаты расширяют круг данных в области гидродеароматизации моторных топлив, особенно превращений ароматических углеводородов в циклоалканы.

Ключевые слова: гидрирование, бензол, жидкая фаза, реактор, родий, катализатор, циклоалкан.

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