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US PURIFIED SOIL FROM SLUDGE
AS A CATALYST CARRIER

Abstract. In this article is consideredusing purified clay from oil sludge and utilize it as carrier of catalyst. Purified clay was converted to pillar structural form by polyhydro-complexes of aluminum chloride and was used to obtain rhodium catalyst containing nickel. Storage the hydrogen in the form of methylcyclohexane was carried outby hydrogenation of toluene in liquid phase at presence of rhodium support catalystwhere as carrier is used pillar structural purified clay. The degree of using an internal surface of porous system is depended.of the size particles.

Keywords: hydrogen, toluene, methylcyclohexane, rhodium, nickelcatalyst, poly-hydrocomplexe, pillar structure, purificated clay.

Introduction. When oil is produced, strong contamination of soil and water with drill cuttings containing hydrocarbons, and oil spills during its extraction are associated with a number of negative phenomena leading to "oiled" and degradation of the soil of huge areas. Naturally, after such an impact, the useful properties of the land are disturbed and require restoration, that is, remediation. Reclamation is a complex of measures aimed at restoring the former fertile qualities of the land, its biological and economic value, as well as improving the environmental conditions. The creation of a high-performance technology for processing oil-contaminated soils will solve the problem of their complete elimination with the return of land to the user, reduce environmental pollution and enable rational use of purification clay from waste [1, 2]. One of the way utulise-thepurification clay from oil sludgeusing them as carrier of catalyst at hydrogenation for storage hydrogen in the form as organic compound. Well known hydrogen is used in the production of various organic substances,in various industries [3]. Hydrogen is one of the environmentally friendly universal energy carrier in the transformation of energy with its participation. The technology of hydrogen production is simple and have an almost unlimited resource base. When introducing technologies of electrocatalytic production of hydrogen from water and the parallel formation of oxygen in the long term will open up the possibility of obtaining thermal energy from a cheap source. However, the low temperature of its liquefaction, the explosion hazard of gaseous hydrogen in case of non-compliance with safety regulations bring to the fore the problems of developing efficient and safe hydrogen storage systems. In our opinion, precisely *these* problems hinder the development of hydrogen energy and technology.

In accordance with the classification of the US Department of Energy, hydrogen fuel storage that use physical processes belong to the first group, and the use of 127torag-chemical processes are chemical methods, where hydrogen is in the form of a chemical compound or in special combinations with the medium of the material. The first group includes the conversion of gaseous hydrogen to a compact state in liquid form in cryogenic containers.Physico-chemical methods use storage by adsorbents (zeolites, activated carbon, hydrocarbon nanocomposites, etc.) and in the form of chemical compounds (alonates, organic and inorganic hydrides, etc.). At the same time, the development of economically viable catalysts for the decomposition of hydrogen-containing compounds, such as water, ammonia, methane, cyclohexane or polyethylene into hydrogen and into the corresponding compounds are promising in hydrogen energy. The main focus of [4] was the investigation of hydrogenation of aromatic hydrocarbons on bimetallic Pt-Pd putting on USY zeolitecatalyst. In [5-7] are considered ways of obtaining sulphur resistant catalysts where metal atoms of support catalysts are modified by alloying, changing the metal particle size, or, changing the acid-base properties of the carrier. The researchers have focused their attention on the high sulphur tolerance of Pt, Pd or bimetallic PtPd on oxide aluminum, dioxide titanium and dioxide silica. Evidently, interest on bimetallic systems are increasing, because they show high selectivity and resistance at poisoning as well as improved activity and stability as confirmed by certain industrial processes [8]. Besides, the patent literature show that the combination of platinum and palladium, putting on alumina and zeolites, is effective for the hydrogenation of aromatic hydrocarbons in petroleum feedstocks containing sulfur compounds [9]. Also, here pointed out that the coexistence of the Pt and Pd in USY zeolite strongly enhances tetralin hydrogenation and improves sulfur tolerance, which depends on the Pd/Pt ratio and reaches a maximum value at a Pd:Pt molar ratio of 4:1 [10]. Bimetallic Pt-Pd putting on a silica-alumina substrate were studied to determine whether the sulfur tolerance of Pt improves when a second noble metal- Pd- is added to a carrier [11]. This silica-alumina substrate selected instead of zeolites in order to minimize the effect of coking on catalyst deactivation.

There are researches about catalytic hydrogenation with platinum metals such as Pt, Pd, Ru, Rh and their bimetallic systems but noble metals easily poisoned by a small amount of sulfur [12-17]. Recent studies have dealt with how to improve the activity of these catalysts and there sulfur resistance by adding another transition metal or using different support material. In the past few years native clays have been developed to prepare various porous pillared adsorbents and support systems for hydrogenation aromatic compounds [14, 16-21]. However, natural clay, bentonite, loses their porosity at heating above the 373K and has a little surface area. One of the possible way of preserving the porosity at heating of clay, is acidity treatment or giving for them pillar structural form. It is possible including supports between layer spaces of clay and named "Layered silicates with support" [18-21]. This material with pillar structural form have significant potential for application in industry, particularly, in petrochemistry, but there are

few studies of these types of materials. It was an incitement to develop the methods of their synthesis and research catalytic properties of modified clays. For obtaining pillar structural clays often used to polyhydrocomplexes of aluminum, transitive metals or organometallic compounds [19-21]. Analyzed having materials we decided to modify purification clay by polyhydrocomplexe of aluminum and use it as carrier for preparation support catalysts. The present work focuses using the intercalated purificationclay as carrier of Rh-Niand studying it as catalyst at the hydrogenation of aromatic compounds for storage hydrogen.

EXPERIMENTAL PART

The purified clay was collected from the "OzenmunaiGas" region Western Kazakhstan. The chemical composition was measured in weigt %: (SiO_2) 54.0-56.0, (Al_2O_3) 18.0-24.0, (Fe_2O_3)6.0-7.0, (MgO) 1.0-2.0, (Na_2O) 1.0-2.0, (H_2O) 9.0-10.0, and other organic ingredients 1.0. Cation-exchange is 64 mmol/100.0g clay. Aliminum (III) chloride, sodium hydroxide were of analytical grade, and used without further purification to prepare molybdenum polyhydrocomplexe. Other chemical reagents $RhCl_3 \cdot 2H_2O$ and $NiCl_2 \cdot 2H_2O$ were of analytical grade. Acidity of environment supervised by means of digital pH meter OP-208/1. Concentration of acids is varied from 0.5 mol/L to 3.0 mol/L.

X-ray diffraction samples were measured using a Rigaku D/Max 2200 VPC powder diffractometer with CuK_α radiation, accelerating voltage of 40 kV, emission current of 30mA, and scanning speed of 10^0/min was used to determine the crystal phase composition of the prepared carrier at 20^0C.

The textural properties of the support catalysts were evaluated from the N_2 adsorption-desorption isotherms obtained at 77K over the whole range of relative pressures, using a Micromeritics ASAP-2000 apparatus. Specific surfaces of catalysts calculated from these isotherms using the BET method in the 0.005-0.25 P/P_0 range. Temperature – programmed study catalysts were carried out in a semiautomatic Micromeritics TPD/TPR 2900 apparatus interfaced to a computer. Amount of Rh and Ni on support catalysts were determined using a Perkin-Elmer 3030 atomic absorption spectrophotometer. The analysis of reaction products were spent by chromatograph Chrom-4. Length of a column is 3 m, diameter – 3 mm filled by firm carrier « Chromaton-N» processed with liquid phase «Poly-ethylenglycoladipate» (15 wt.% of the carrier). Temperature of a column 373K, temperature of the evaporator 423K. Carrier gas – argon, velocity of the carrier gas – 50 cm^3/min.

Preparation of pillared clays carried out as in [20, 21]. Suspension of puri-ficated clay prepared in water and mixed up during 6 h, pH-water extract of clay makes ~ 8-9. The polyhydroxocomplex was obtained by adding gradually the solution of sodium hydroxide to aqueous solution of aliminum (III) chloride. Concentration of aliminum (III) chloride change from 5.0 to 30.0 mmole Al^{3+} per gram clay. For prevent from coagulation of the solution polyhydroxocomplexes of aliminum it slowly added to suspension of clay. After endurance this system

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during the 24 h, a deposit was washed by water and condensed. The paste after separating from a liquid phase undergoes to dry at the room temperature (48h), then at 110^0C for 2h with the subsequently rising the temperature up to 160^0C (4h). After cool off it to the room temperature a firm mass was pounded to a powder and sifted to different fractions with the certain sizes of particles. Fractions of pillar structural bentonite with particles of the size less 2.0 mm was impregnated by aqueous solutions of $RhCl_3 \cdot 2H_2O$, then $NiCl_2 \cdot 2H_2O$ at room temperature. Subsequently, from suspension was evaporated water at mixing, then obtained paste was dried at 120^0C in air for 6 h and finally calcinated in air at 300^0C for 4 h. The amount of Rh and Ni containing on the pillar structural clay were changed from 0.1 to 1.0 wt. %. A molar ratio Rh:Ni is varied from 1:1 up to 9:1. Before experience the pattern of the catalyst about 0.1g was reduced in the stream of hydrogen (50 cm^3/min) at a heating rate 4^0C/min up to a final temperature 350^0C and kept at this condition for 2 h. After reduction the catalyst was cooled to room temperature in the same flow of hydrogen and under a layer of n-hexane was transferred to a steel autoclave (working capacity 100 cm^3) which supplied by mixer and interfaced to a computer. For hydrogenation had taken 50cm^3 mixture of aromatic hydrocarbon and n-hexane [V(arom.):V(n-hexane) = 1:1]. Dilution by n-hexane made for dispersion of heat allocated at hydrogenation and aspiration process to spend in conditions of ideal mixture. In order to determine resistance of developing Rh-Ni/Carrier at hydrogenation used toluene containing sulfur compounds such as thiophene – 0.04 wt.%. The range of the applied process parameters – temperature, pressure and amount of catalyst based on the results of preliminary experiments.

Initial rate of hydrogenation was defined from the change concentration of aromatic hydrocarbon due to of time. The hydrogenation of aromatic hydrocarbons carried out on the 0.1-1.0wt.%RhNi/Carrier at temperatures in the range of 100–180^0C, and H_2 inlet partial pressures of 0.4-4.0 MPa.

RESULTS AND DISCUSSION

Modifying purified clay by polyhydroxocomlexes Al(III) leads to growth of a specific surface from 66 up to 260 m^2/g, total volume of porous from 0,18 cm^3/g up to 0.54 cm^3/g, interlaminar distances from 0.90 up to 2.04 nm.

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

The maintenance of ions, mmole/g.clay	S, m^2/g	d_{001}, nm	Total volume of porous, cm^3/g	Loss of thermostability	
				T, °C	S_{SP}, m^2/g
–	66	0.94	0.16	140	20
5	130	1.24	0.44	360	80
10	160	1.58	0.48	440	110
15	240	2.02	0.54	500	220
20	260	2.04	0.56	560	240
30	240	1.90	0.53	500	230

The maximal distance 2,00-2,04 nanometers corresponds to concentration of aluminium about 15-20 mmole per gram of clay where between the layers settle down polyhydroxocomplex ions.ncrease the concentration of aluminium 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 forms of aluminium chloride which do not influence formation pillar structures. At first defined influence of an internal surface of the catalysts to the hydrogenation rate of aromatics. For it a criterion Tyle – Zeldovich "φ" was calculateded, which described by following formula[19]:

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

where R_0 is the resulted radius of particles of the catalyst (for spherical particle $R_0 = R/3$, R - radius of sphere), k is a constant of rate of reaction; D is an 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 cm^2/sec., and for liquid molecular diffusion 10^{-5} cm^2/sec. [22]. On their datum, the factor of diffusion for gas dissolved in a liquid has the same order, as for the liquid of 10^{-5} cm^2/sec. At 120°C saturated vapor pressure of toluene, is 2 bar. Fugacity (*f*) of toluene vapor in this condition is ~ 0.80 *atm.* Activity coefficient of liquid toluene at 393K and 40 bar is equal 0.95. At common pressure of system 40 bar fugacity of toluene is equal ~ 38 *atm.* It also related to derivatives of toluene, which have high boiling temperature. Constant of rate hydrogenation of aromatic hydrocarbons were defined at presence of a powder support catalyst with the average size of particles about 0.05- 0.2 mm. The factor of efficiency – a degree of use of an internal surface is calculated from the relation thφ/φ, and the value of thφ calculated by equality:

$$th\varphi = [exp\varphi) - exp(-\varphi)] / [exp(\varphi) + exp(-\varphi)].$$

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

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 (H_2) = 40 bar., C(toluene) = 2.8 mol/L

The average size of diameter of particles of the catalyst, mm	φ	th φ	thφ/φ
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

Data of table 2 shows, that using the catalysts with average diameter of particles 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.

The main objective of the present work was to determine whether the sulfur toleranceof Rh improves when a second transition metal Ni is added to a pillar structural bentonite containing compounds of aluminium. Experimental data confirmed that the coexistence of Rh and Ni on "Carrier" strongly enhances benzene hydrogenation and improves sulfur tolerance, which depends on the Rh:Ni ratio and reaches a maximum value at a Rh:Ni molar ratio of 1:1 in the range of hydrogen pressure 1.0-4.0 MPa and temperature 100-180 °C. Conversion of toluene to methylcyclohexane (80.0 wt.%) is achieved at hydrogen pressure 0.5-1.0 MPa and 120-140 °C. Using one of the same sample of catalyst consecutive ten times for the hydrogenation of benzene its value of conversion not decreased at the containing sulfur about 0.04 wt.% in the origin benzene. It shows that hydrogen can be storage in the toluene as methycyclohexane. At the same time the conversion of mesitylene is about 58 wt.% accordingly. This value for p-xylene, o-xylene and m-xylene are 36; 28 and 27 wt.% accordingly. All these results show that developed RhNi support catalyst is stability against to poisonous sulfur compounds and may be used for storage hydrogen in toluene as methyl-cyclohexane. Apparently, the sulfur tolerance of this system was attributed to structural and electronic effects. Studies [23] revealed that PtPd catalyst form alloyed clusters, as well as the dispersion of metals strongly affect the activity as well as the sulfur tolerance of bimetallic catalysts. In contrast, the ability of metals to form bulk alloys is not a necessary condition for their use as catalysts [24-27]. The high sulfur resistance of the Pt-Pd was attributed to structural and electronic effects rather than to the degree of metal dispersion[7]. However, the authors in future carry out experimental evidence of the structural and electronic modifications.

Conclusion. It is shown using purified oily soil as catalyst carrier at hydrogenation aromatic hydrocarbons for storage hydrogen in the form organic compounds.The range of the applied concentration of RhNi based on the results of preliminary experiments had shown increasing their activity from 0.1 to 1.0wt%. The further increase of RhNi above 1.0wt% insignificantly influence on activity of catalyst. It indirectly shows that catalytic activity dependent on of metal dispersion and its oxidation number. Therefore, the combination of Rh and Ni metals with pillar structural clay intercalated by Al compounds gave possibility to display them both properties- catalytic activity for hydrogenation of aromatic hydrocarbons and resistance to sulfur compounds.

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Резюме

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МҰНАЙ ҚАЛДЫҚТАРЫНАН ТАЗАРТЫЛҒАН САЗДЫ КАТАЛИЗАТОР ТАСЫМАЛДАУЫШЫ РЕТІНДЕ ПАЙДАЛАНУ

Аннотация. Келтірілген мақалада мұнай қалдықтарынан тазартылған саз топырақты катализатор тасымалдағышы ретінде қолдану қарастырылған. Тазартылған саз топырақ кеуектіқұрылымға алюминий полигидрокомплексі көмегімен түрлендірілді. Алынған тасымалдауышқа родий және никель қосылыстары отырғызылып, толуолдың құрамында сутегіні метилциклогексан түрінде сақтау ұсынылды.

Гидрлеу реакциясы сұйық фазада жүргізілді. Катализатордың ішкі кеуек қуысын пайдалану оның түйірлерінің ірілі ұсақтығына тәуелді.

Түйін сөздер: сутек, толуол, метилциклогексан, родий, никель, катализатор, полигидрокомплекс, кеуекті құрылым, тазартылған саз топырақ.

Резюме

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ИСПОЛЬЗОВАНИЕ ОЧИЩЕННОГО ГРУНТА ОТ НЕФТЕШЛАМА В КАЧЕСТВЕ НОСИТЕЛЯ КАТАЛИЗАТОРА

Рассматривается использование очищенной глины от нефтешлама и использование ее в качестве носителя катализатора. Очи-щенная глина была преобразована в столбчато-структурную форму с помощью полигидрокомплексов хлорида алюминия и использовалась для получения родиевого катализатора, содержащего никель. Хранение водорода в форме метилциклогексана осуществляли гидрированием толуола в жидкой фазе в присутствии родиевого катализатора, где в качестве носителя использовали столбчато-структурную очищенную глину. Степень использования внутренней поверхности пористой структуры родиевого катализатора, содержащего никель, зависит от размера частиц.

Ключевые слова: водород, толуол, метилциклогексан, родий, никель, катализатор, полигидрокомплекс, столбчатаяструктура, очищенная глина.