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Study of catalytic activity of modified montmorillonite sustainable in supercritical water

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Abstract. Currently, the world is intensively exploring the possibility of obtaining highly active catalysts for hydrothermal processing of high-viscosity oils through the synthesis of new carriers, optimization of the composition, structural parameters in order to increase the degree of conversion of high-molecular hydrocarbons. The work is devoted to the study of the composition and properties of a montmorillonite intercalated with $\gamma\text{-Al}_{13}\text{O}_4(\text{OH})_{24}(\text{OH}_2)_{11}(\text{OH})_6^+$ and containing catalytically active pillars agents $\gamma\text{-Al}_2\text{O}_3$ in the reactions of hydrothermal transformation of high-viscosity oils. Experiments conducted in a catalytic laboratory setup in a flow-down reactor with a stationary layer of pillared montmorillonite at a temperature above 450 °C and a pressure of not more than 0.5 MPa showed an increase in the conversion of high molecular weight n-alkanes 1.3 times, with the formation of low-boiling n-alkanes and alkanes branched structure.

1. Introduction

To date, Russia sharply raised the issue of the production of highly active catalysts of deep processing of high-viscosity oil, corresponding to world level [1-4]. Poor quality or complete lack of modern domestic highly active catalysts, together with the negative trend of the foreign producers focused on the import is not the most modern brands catalysts, constrained by high pace of development of high-viscosity oil in the Republic of Tatarstan and the Russian Federation. Leading manufacturers improve technology of highly active catalysts due to the synthesis of new carriers, optimization of the structural parameters and the stability of the catalyst to deactivation in order to increase the degree of conversion of high-molecular hydrocarbons of petroleum.



The work is dedicated to study of composition, properties and the catalytic activity is stable in supercritical water, modified montmorillonite in the hydrothermal conversion reactions of high-viscosity oil.

Layered silicates have a two-dimensional channel system zeolites and comparable to increase the availability of the hydrocarbon molecules in the interlayer space. The introduction of the silicate layers of certain cations Keggin, may increase the channel, making them wider than zeolites, that makes pillar clays convenient carrier for the active components of catalysts cracking large hydrocarbon molecules highly viscous oils, which cannot penetrate the pore system of zeolites. The acidic nature of the layered silicate is caused by the presence of Johannes Nicolaus Bronsted centers, which are proton donors, and Lewis is an electron acceptor pair. The presence of Lewis Center provides pillar agents. Due to the acidic properties of silicate can be used in the cracking reactions, hydroisomerization, dehydration, dehydrogenation, hydrogenation, aromatization, disproportionation of hydrocarbons. The most common metals for the intercalation into the interlayer space of the clay materials are Al, Zr, Cr, Fe and Ti [5, 6]. The object of investigation is selected selected from bentonite intercalated montmorillonite pillar agent is a Keggin (Al_{13}) – $\gamma\text{-Al}_{13}\text{O}_4(\text{OH})_{24}(\text{OH}_2)_{11}(\text{OH})_6^+$. This complex is composed of 12 octahedral Al^{3+} ions and a central tetrahedral Al^{3+} .

2. Methodology

The modified layered silicate is prepared in two stages. First, polyhydroxocation intercalation into the interlayer space of montmorillonite aluminosilicate with negatively charged layers, the second: heat treatment intercalated silicate. As a result of the heat treatment hydroxocations Al_{13} , embedded into the interlayer space of the silicate layers are transformed into $\gamma\text{-Al}_2\text{O}_3$, which create columnar periodic system and stitching silicate layers form a nano porous structure. The elemental composition of the obtained using energy dispersive X-ray fluorescence spectrometer, at the final stage after calcination montmorillonite contained more than 18 % $\gamma\text{-Al}_2\text{O}_3$. Textural characteristics were investigated by thermal desorption of nitrogen, the specific surface area calculations performed according to Brunauer-Emmett-Teller effect. The intercalated montmorillonite is characterized by the nanoporous structure, high specific surface area greater than $0.8 \text{ cm}^2/\text{g}$ and a pore volume of $5\text{-}20 \text{ nm} \sim 0.42 \text{ cm}^3/\text{g}$. Phase composition of montmorillonite before and after implementation has been investigated by a powder X-ray diffractometer, the basal spacing after calcination was $\sim 1.3 \text{ nm}$. To study the changes occurring on the surface of montmorillonite used scanning electron microscopy.

Pre-catalytic activity of the modified montmorillonite during hydrothermal exposure was studied using a model mixture of high n-alkanes with different geometric characteristics in a laboratory setup catalyst flow type. Installation equipped with a pre-heated raw material container with a stirrer, feed lines pumps the mixture of the evaporator, gas lines nitrogen supply installation, an evaporator, a tubular reactor with a fixed bed of the modified montmorillonite exchanger-condenser for the final reaction products, a backpressure regulator, a separator for separating products reaction [7]. The reactor temperature was 450°C , in the evaporator 400°C , pressure 0.5 MPa. The yield of the operating temperature

was carried out in nitrogen flow at identical temperatures in the evaporator and reactor. The temperature in the heat exchanger-condenser ~ 10 °C. Yield on predetermined setting mode carried out in a nitrogen stream, and then nitrogen feed was stopped, and feeding of the starting mixture of n-alkanes at a rate of 0.5 ml / min, the volume ratio of n-alkanes to the volume of the modified montmorillonite oxide was 9:1 hour⁻¹. According to X-ray fluorescence analysis after catalysis content of γ -Al₂O₃ in pillars silicate has changed. On a sample of the modified montmorillonite before and after catalysis of any other independent phases was observed. It should be noted that the catalysis of higher n-alkanes in the presence of the modified montmorillonite at 450 °C does not lead to an increase in the content of carbonaceous substances, but significantly increases yield gaseous products from 14 (control) to 17 wt %. Analysis of the gaseous products of the cracking of n-alkanes was conducted by gas chromatography. The composition gases are methane and propane to 35 wt %, as well as butane, iso-butane, pentane. From the literature it is known that an increase in cracking temperature linear alkanes ~ 500 °C while maintaining the atmospheric pressure increases the yield of the product gas with high selectivity to ethylene and propylene.

3. Results and Discussions

Analysis of the micrographs shown in Figure 1, leads to the conclusion that the surface is characterized by a pronounced relief formed aggregates of rounded grains no larger than ~ 200 nm. After calcination, the surface of the relief is smoothed, and the obvious changes in the composition of the grain size of the aggregates is not observed, but the degeneration of their contact boundaries occurs.

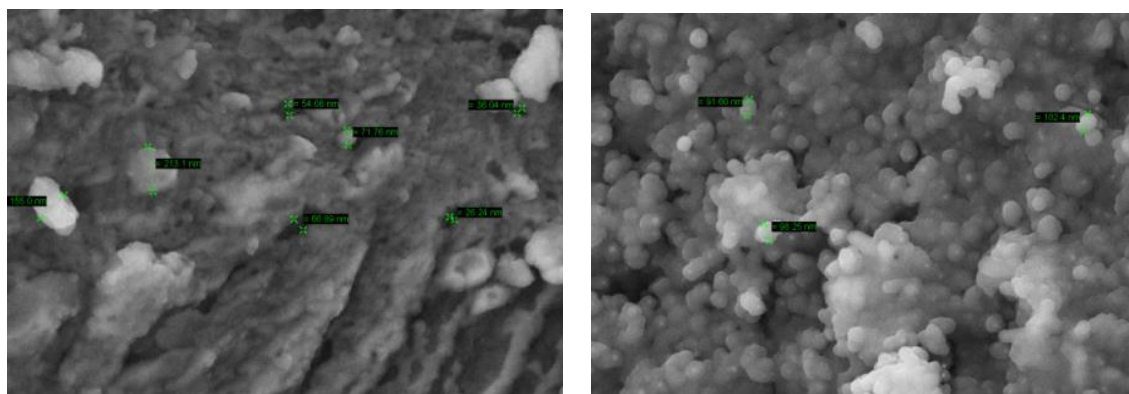


Figure 1. Microstructure of the surface.

Analysis of the composition of liquid conversion products was carried out by chromatography and mass spectrometry using gas-liquid chromatography-mass spectrometer PerkinElmer Turbo Mass Gold GS/MS. Separation was conducted on a capillary column 30 m long, 0.32 mm diameter with PE-XLB phase, carrier gas - helium flow rate of - 2 ml/min. Impact modified montmorillonite in the composition of the liquid product illustrated data table. Note that, in the presence of the modified montmorillonite degree of conversion of n-

alkanes is increased by more than twice. Parallel isomeric cyclization may go carbocation, a structure which is desorbed to form methylcyclopentyl (Table 1). Cycloolefin further adds hydrogen to the metal center of the catalyst, turning to methyl cyclopentane. The resulting olefin further adds hydrogen to form cyclohexane or cleaves hydrogen to benzene. In turn, benzene is reacted with alkenes formed during disproportionation of n-alkanes. This is supported by the presence in the reaction mixture of alkylbenzenes.

Table 1. The difference in the composition of newly formed hydrocarbons in the products of the control experiment and cracking of n-alkanes in the presence of modified montmorillonite.

Control experiment		Product experiment	
Component	content, wt %	Component	content, wt %
hexane	0.1764	hexane	0.1052
heptane	0.3386	heptane	0.1762
3-methyl-2-ethylhexane	0.1186	3- ethylhexane	0.3081
3-methylheptane	0.4981	octane	0.2824
3- ethylhexane	0.3842	cis-1,2-ethylmethylcyclopentane	0.1249
octane	0.1415	o-xylene	0.6329
2,4-dimethylheptan	0.1099	nonane	0.5649
3-methyloctane	0.7527	2,5-dimethyloctane	0.1266
o-xylene	0.2379	1-methyl-3- isopropylcyclohexane	0.7867
nonane	0.4581	1-methyl-4- isopropylcyclohexane	0.2586
2,5- dimethyloctane	0.1348	decane	0.5899
1-methyl-2- butylcyclopentane	0.8236	1,2,3- trimethylbenzene	0.1298
1-methyl-3- isopropylcyclohexane	0.1944	1-ethyl-2-i- <u>propylbenzene</u>	0.8945
decane	0.4694	4- <u>undecene</u> (e)	0.1357
1,2,3-trimethylbenzene	0.1322	6-dodecene (z)	0.2765
1-ethyl-2-i- <u>propyl benzene</u>	0.9113	2-methyl decane	0.5464
3-methyl undecane	0.1030	1-butyl -2-pentyl cis-cyclopropane	0.8626
6- dodecene (z)	0.2230	3-dodecene (e)	0.1218
1-butyl -2-pentyl cyclopropane	0.8124	Tridecane	0.4116
1-ethyl-4,2- methylpropylbenzene	0.1324	1-tetradecene	0.3970
2- methyldecane	0.4863	tetradecene	0.3641
tridecene	0.2987	cis-2-methyl-7-octadecene	0.3287
1- tetradecene	0.3607	7-hexadecene	0.1120
tetradecane	0.2600	octadecane	0.1048
cis-2-methyl-7-octadecene	0.4767	nanodecane	0.1079
3-ethyl5-(2-ethylbutyl)octadecene	0.1134	2-methyl -eicosane	0.2986
2-methyl-7-hexadecene	0.1062	2-methyl-7-nondecane	0.6633
2-methyl-eicosane,	0.1436	4-methyldocosane	0.2030
2-methyl-7-nondecane	0.3569		
10 methyl-eicosane	0.2068		

Symbatically the conversion increases alkyl-substituted benzene selectivity (from 23 to 33 wt %), while the cumulative selectivity to aromatics practically unchanged (45.3 and 45.6 wt %) (Figure 2). Along with the progress of the aromatization reactions in the system tested side cracking and disproportionation reaction resulting in the formation of mono- and di-olefins and naphthalene derivatives, which subsequently take part in the coking reactions in the absence of excess hydrogen in the reaction medium.

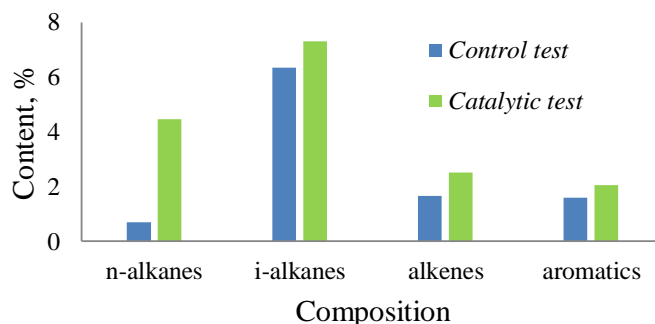


Figure 2. Group composition of new formed hydrocarbons in the final experimental products.

This is supported by, in particular, the reduction of the integral output diene. For the intended transformation circuit of n-alkanes in the first step occurs at dehydrogenation γ - Al_2O_3 centers of montmorillonite to form dienes. In chemisorption dienes in a protic acidic center formed carbonium ion is subsequently isomerized to a stable structure alkanes branched structure.

Conclusions

Studies have shown that the silicate intercalated with hydroxocations γ - $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{OH}_2)_{11}(\text{OH})^{6+}$, embedded in the interlayer space, after calcination contains 18 % γ - Al_2O_3 and has a nanoporous structure with a volume of $\sim 0.42 \text{ cm}^3/\text{g}$, as well as a specific surface area of more than $0.8 \text{ m}^2/\text{g}$. The experiments carried out on a catalytic unit in a flow-down reactor with a stationary layer of modified layered silicate at a temperature above 450°C and a pressure of not more than 0.5 MPa showed an increase in the degree of conversion of high-molecular n-alkanes of high-viscosity oils by 1.3 times, with the formation of low-boiling n-alkanes and alkanes of a branched structure. According to x-ray fluorescence and x-ray spectral analyses, the elemental and phase composition of intercalated layered silicate does not change before and after catalysis.

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