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Catalytic Effects Research of Carbonaceous Rock under Conditions of In-Situ Oxidation of Super-Sticky Naphtha.

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ABSTRACT

Micro-structural features and structures of carbonaceous rock under the influence of hexane transmutation products in model thermocatalytic system are studied. It is established that in the air-oxygen environment in presence of the cobalt and carbonaceous rock catalyst – acetylacetonate at a temperature of 200 °C high molecular weight destruction processes take place in heavy naphtha with a new forming of light hydrocarbons. In the research the influence of hexane in the presence of Co[acac]$_3$ on carbonaceous rock is revealed. Due to formation of the oxygenated products containing carboxyl groups there is a calcite destruction that it is possible to consider as positive moment. However, according to microscopic researches results, in practice, with use of heavy naphtha fine-grained carbonaceous connections, which can lead to time and deterioration colemating of filtrational and capacitor collector properties are formed. Presence of light hydrocarbons as a part of the studied research products shows destruction of naphtha high molecular weight components. We studied the micro-structural features and compositions of the carbonate rocks under the influence of transformation products hexane catalytic thermal model system. It is established that in the air-oxygen environment in the presence of catalyst - acetylacetonate and cobalt carbonate rock at 200°C decomposition processes occur in macromolecular components of the heavy oil with a light hydrocarbon neoplasm.

Keywords: thermocatalytic oxidation, carbonaceous rock, cobalt (III) acetylacetonate, heavy naphtha, hydro-carbonic structure.

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INTRODUCTION

Considering the larger share of naphtha reserves in carbonaceous collectors, relevance for hydro-carbonic raw materials stocks development by thermal methods has large production potential [1-7]. Naphtha concentrated in carbonaceous rocks usually fall into hard mining hydro-carbonic resources, and deposits - to difficultly constructed collectors with low filtrational and capacitor characteristics [8]. By chemical composition heavy naphtha represent the complex mixtures of high molecular weight hydrocarbons and their derivatives containing sulfur, oxygen, nitrogen, as well as metals generally vanadium, nickel, iron, magnesium and chrome, their density varies from 0.96 to 1.08 g/cm ^{3}, viscosity from thousands to hundreds of thousands centipoise and more. The main component of the petrocontaining carbonaceous rock is calcite, in slight quantities there are adamant, magnesium, silicon, iron and titanium dioxide.

Features of native bitumen bedding, their abnormal viscous and other physical and chemical characteristics in most cases make the methods used for development of routine oil fields inefficient. The special attention is paid to development of heavy naphtha in-situ oxidation methods. The technology means downloading in layer of air or air-oxygen mix, with delivery in catalyst layer, allowing, if necessary, the local layer to heat. Carrying out catalytic low-temperature oxidation of naphtha demands maintaining the layer temperature within 150-270 °C at which initiation of oxidizing reactions of petroleum hydrocarbons with use of homogeneous or heterogeneous catalysts [1, 2] is possible.

The current research is devoted to actual problem of production bound to heavy hydro-carbonic resources, namely identification of the changes happening in petrosaturated carbonaceous rock under the influence of homogeneous oxidation catalyst in the oxygen-air environment.

RESEARCH METHODS

As homogeneous hydrocarbons oxidation catalyst the Tris(acetylacetonatol) Iron(III) - Co[acac]$_3$ is used. Experiment were carried out in the laboratory batch reactor made of stainless steel in the air-oxygen environment. The thermobaric parameters of experiments and characteristic of termination products are specified in table 1. Cobalt (III) acetylacetonate influence study on carbonaceous rock for hydrocarbons accelerating oxidizing reaction is interesting because catalyst is responsible for numerous oxygen-bearing chemicals formation. The carboxylic acids which are formed thus are capable to destroy carbonaceous collector. To reveal influence of Co[acac]$_3$ on carbonaceous rock, at the first stage, as the simplified model of naphtha hexane mix with a small amount of benzene was used. At the second stage, the object of research was served by the heavy high-viscosity naphtha extracted from carbonaceous rock of Devon and average carbon fabrics on the known Paro technology - gravitational impact on layer. Naphtha is extracted on the Ashalchinsky field of the Tatarstan Republic from depth of 110 m from a day surface.

RESULTS AND DISCUSSION

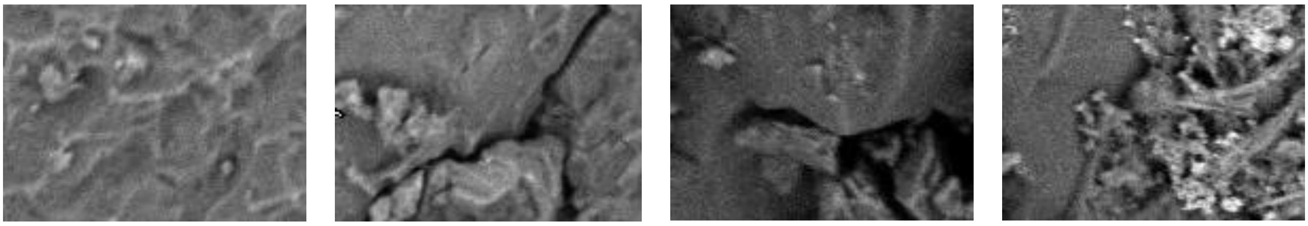
Table 1: Technological experiment parameters, density of the received products

Original stock structure in experiments	Temperature, °C	Pressure, MPa	Density, at 20 °C, kg/cm^3
Carbonate: hexane (1:1), *Co[acac]$_3$ 2.0%*	200	5.0	0.6643 (*hexane)*
Carbonate: hexane (1:1), *Co[acac]$_3$ 2.0%*	200	8.0	0.6660 (*hexane)*
Carbonate: hexane (1:1)	200	8.0	0.6588 (*hexane)*
Hexane (1:1), *Co[acac]$_3$ 2.0%*	200	5.0	0.6627 (*hexane)*
Carbonate: naphtha: hexane (1:1:1), *Co[acac]$_3$ 2.0%*	200	5.1	0.9463 (naphtha*)*
Naphtha: hexane (1:1), *Co[acac]$_3$ 0.5%*	175	0.4	0.9715 (*naphtha)*
Carbonate: naphtha: hexane 1:1:1	250	1.4	0.9147 (*naphtha)*
Carbonate: naphtha: hexane: water (1:1:1:1), *Co[acac]$_3$ 2.0%*	250	2.0	0.8969 (*naphtha)*

In the first and second experiments on identical structure of original stock (carbonate, hexane, Co[acac]$_3$) pressure was increased from 5 to 8 MPas, thus in experiment with higher pressure density of fluid products increased, this can testify that pressure boost leads to formation of high-molecular compounds. To exclude influence of micro-impurity of calcite on hexane transformation, experiment of calcite with hexane in the ratio 1:1 during which it was revealed that density of resultants of reaction in comparison with hexane density (0.6548 g/cm ³) was higher, it is possible to make the assumption that these products contain oxidized and, perhaps, the flavored connections. Thus, it is possible to assume that carbonaceous rock possesses catalytic properties. The carried-out ultimate analysis of calcite indicates the contents in slight amounts of group (Ni, Fe) metals VIII, capable of showing the hydrogenating and dehydrogenating properties.

For detection of micro-structural features in change of carbonaceous rock mineral structure researches on Philips XL-30 company for raster super-microscope with the micro-probe analysis were conducted on optics microscope (on EDAX spectrometer). Images of calcite change after carrying out experiments are given in figure 1. As we can see on the pictures, the calcite practically did not change after experiment with hexane. In experiment with addition of Co [acac] ^{3} rock change is observed, and with addition of naphtha formation of carbonized substances is noticeable. Thus the amount of carbonized substances decreases when carrying out experiments with hexane and Co[acac]$_3$ while at addition of heavy naphtha their quantity increases, this proves that calcite can act as a germ in termination products of experiment carbonized components.

The element structure of carbonate and formed carbonaceous substances was determined by method of their burning on semi-automatic C, H, N analyzer. According to the ultimate analysis of calcite, in its structure in small amounts there are 10% carbon, silicon, aluminum, iron, and also nickel and vanadium. In experiments on carbonate with hexane and Co[acac]$_3$, structure and amount of the specified metals in the transformed rock changes slightly, carbon content decreases. Addition of naphtha into described structure of original mixture leads to increase in the contents of carbon carbonate that is caused by adsorption of formed carbonaceous substances on its surface. The ultimate analysis of carbonaceous substances indicated traces of metal in their compositions which are present in calcite.



Carbonate

Carbonate, hexane

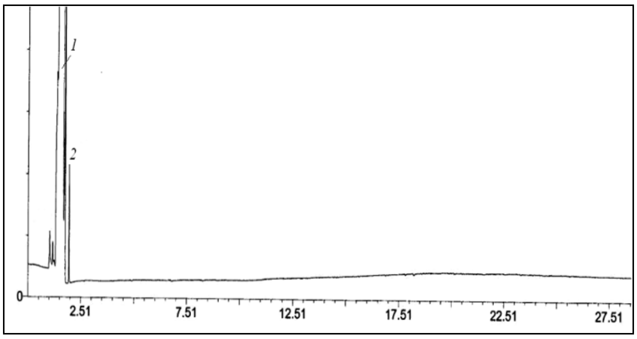
Carbonate, hexane, Co[acac]$_3$

Carbonate, naphtha, hexane, Co[acac]$_3$

Figure 1: Carbonate surface morphology before experiments

The structure of experiment fluid products was researched by a chromatin-mass spectrometry method on the DFS Thermo Electron Corporation device (Germany). We used a capillary column 50 m long, with a diameter of 0.32 mm with the fixed phase ID-BP5X, gas – helium, energy, ionizing electrons made 70 eV. Chromatography was carried put in the mode of the linear temperature programming: from 30 to 280 °C with speed of 10 ° / min. Data processing was carried out using the Xcalibur program. The Chromato-mass-spectrometric analysis of hexane transmutation products (fig. 2) allowed to record a number of oxygen-containing hydrocarbons (tab. 2).

a



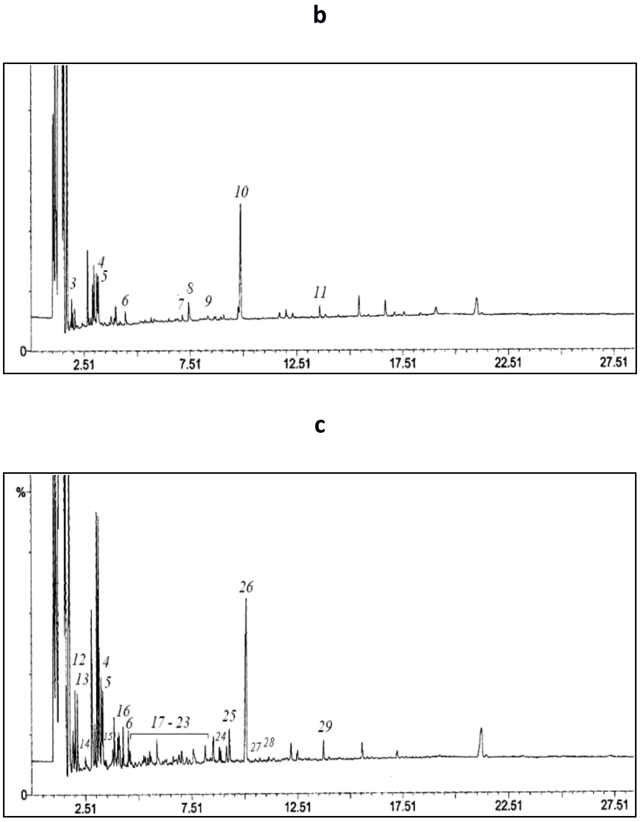


Figure 2: Chromatograms: a) hexane, b) hexane, Co[acac]$_3$, c) carbonate, hexane, Co[acac]$_3$

As it is possible to see from chromatograms, in the chosen thermobaric conditions of experiments, conversion level of hexane is very low, about 10%. In experiments of hexane with Co[acac]$_3$ in termination products various derivatives of benzene are identified, there are hexane oxidates (3-geksanon, 3-metilbutan acid, 2 methyl, 3-pentanon), lengthening and branching of hydrocarbon chain (3,4-dimetilhexan, 5,6-dimetildekan, pyrane derivatives) is also observed. In experiment termination products with carbonate, hexane and Co[acac]$_3$ the maintenance of both oxygenated products, and connections with high content of carbon atoms in a chain is recorded to increase.

Table 2: Hydro-carbonic structure of experiment products

Peak No.	The identified connection
Hexane	
1	hexane
2	benzene
Hexane, Co[acac]$_3$	
3	benzene derivatives
4	3,4-dimetit, hexane
5	3-hexanon
6	2-methyl, 3-pentanon
7	2,7-dimetit, octane
8	3-methyl, butanic acid
9	3-methyl, 4-pentanon
10	5,6-dimetit, dekan
11	pyrane derivatives
Carbonate, hexane, Co[acac]$_3$	
12	2,3-dimetit, pentane
13	3-methyl, hexane
14	furan derivatives

15	2,4-dimetit, hexane
16	4-aethylium, heptane
17	1,2-dimetit, benzylium
18	cyclohexane
19	2,2,4-trimetit, pentanon
20	4-aethylium, octane
21	2,4,6-trimetit, heptane
22	2,3-dimetit, heptane
23	5-methyl, dekan
24	4-methyl, decen
25	2,4,6-trimetit, octane
26	2,4-dimetit, dekan
27	5-aethylium, hendecane
28	naphthalene
29	2-methyl, naphthalene

The conducted researches with naphtha showed that under the influence of thermal and catalytic factors the most essential changes are observed in its component structure (table 3). In naphtha after experiment the exit of light hydrocarbons with boiling point increases to 200 °C. The greatest quantitative decrease is observed in the paraphinonaphten and aromatic hydrocarbons.

Table 3: Experiment technological parameters

Original stock structure	Exit fr. n.k.. -200 °C, %	* Component structure, Mas. %			
		PN UV	Ar. UV	Pitch	Asphaltene
Naphtha, initial	9.8	40.8	13.7	37.8	7.7
Naphtha: hexane (1:1), Co[acac]$_3$ 0.5%	12.1	39.5	11.3	36.9	6.1

* The component structure model boiling above 200 °C

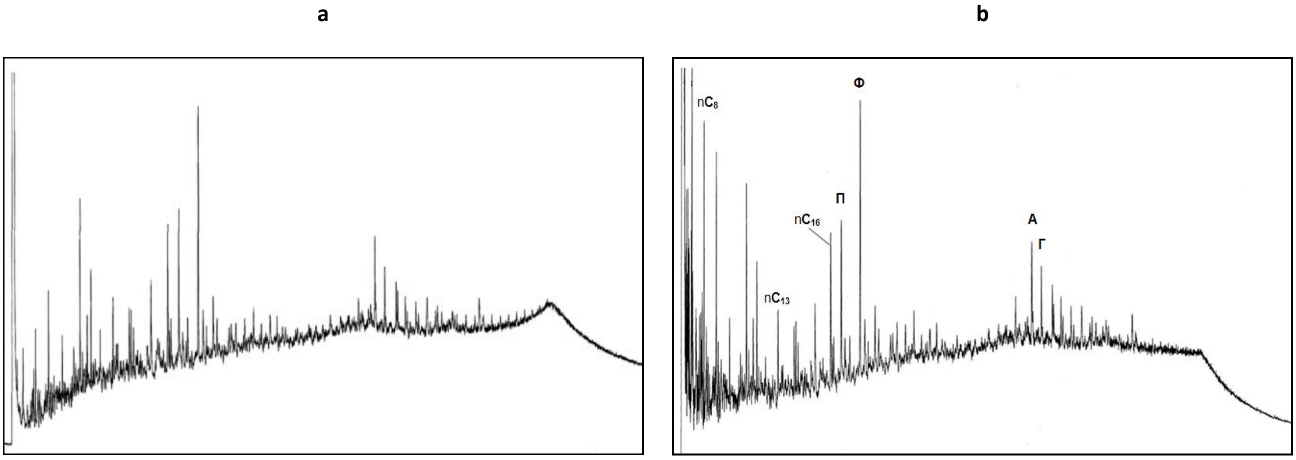


Figure 3: Chromatograms of the transformed naphtha:a) naphtha initial; b) naphtha, hexane, Co[acac]$_3$

In naphtha alcanes of izoprenoid C14-C20 structure among which the maximal concentration is necessary on pristan (C19) and phitan (C20) (fig. 3a) generally prevail, also in its structure the maintenance of high molecular weight terpan is high, adiantyne and hopan concentration in which is maximum. The naphtha conversion product significantly does not differ from initial naphtha on the relative distribution of izoprenoid alcanes, but from the given chromatograms it is visible that in experiment product in more low-boiling area there are intensive peaks of neogenic hydrocarbons among which N alcanes of C7-C12 structure and aromatic hydrocarbons are identified.

During work influence of hexane in the presence of Co[acac]$_3$ on carbonaceous rock was revealed. Due to formation of the oxygenated products containing carboxyl groups there is a calcite destruction that it is possible to consider as positive moment. However, according to microscopic researches results, in practice, with use of heavy naphtha fine-grained carbonaceous connections, which can lead to time and deterioration colemating of filtrational and capacitor collector properties are formed. Presence of light hydrocarbons as a part of the studied research products shows destruction of naphtha high molecular weight components.

SUMMARY

- It is shown that carbonaceous rock possesses catalytic properties. The calcite contains in slight quantities metals VIII of group (Ni, Fe), capable to show the hydrogenating and dehydrogenating properties.
- Under the influence of thermal and catalytic factors the most essential changes are observed in component petroleum composition. The content of light hydrocarbons with boiling point increases to 200 °C. The greatest effect is observed in the paraffin oil and aromatic hydrocarbons.
- Influence of hexane in the presence of $Co[acac]_3$ on carbonaceous rock is established. Due to formation of the oxygenated products containing carboxyl groups there is a destruction of a calcite.

CONCLUSION

Thus, results of the conducted researches showed the main directions of reactions and transformations of hydro-carbonic components of heavy naphtha course in the studied systems, transformation of carbonaceous rock that eventually assumes possibility of Tris (acetylacetonatol) Iron (III) use in technology of in-situ low-temperature heavy naphtha oxidation.

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