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Catalytic Aspects of the Filling of Oil Fields

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Summary

The experimental possibility of the filling of the Romashkinskoye oil field due to the catalytic transformation of methane under the influence of structurally deformed associations of fine particulate clay minerals is presented in the paper.

Introduction

Oil-bearing rock is determined, as is known, the presence of hydrocarbons in the earth's crust and collection tanks. The formation of oil deposits is due to the migration geofluids, as part of which is dominated by hydrocarbons having small geometric dimensions and sufficient chemical inertness, which allows them to avoid the structural and chemical exposure rocks. However, in the composition of oil deposits are present and heavy hydrocarbons from difficult-branched structure, which migrate over long distances is difficult to imagine. Their origin is usually associated with the manifestation of various supergene and thermal-oxidative processes [1]. But there is another way of education, namely, through the catalytic conversion of molecules geofluids.

Minerals are known in nature, possessing catalytic properties. These oxides, metal sulfides , etc. However, the most common are fine clay mineral associations, representing more than 60% of the sedimentary rocks of the Earth 's crust , the catalytic ability which largely depend on the degree of dispersion.

In this regard, the most active clay minerals are formed under the influence of tectonic stress, producing chemical and mechanical ultradispergirovanie mineral components, such as a foundation decompressed zones. Ascending intracrystalline energy secondary educated clays will promote and thermobaric conditions such zones destructions in which they partially lose water and become the deformed structure of infinite order in the form of nano-sized cylinders, spheres, hemispheres [2].

Due to structural defects clay minerals small molecules geofluids can penetrate the interlaminar space weakly bound lattice clay layers. At the same time, increasing the frequency of interaction "guest" with the walls of the layer "host" (rock matrix) into a kind of "nanoreactor" weaken the C-H bond, thus speeding up the process of converting methane to much lower energy costs. One manifestation of this enhanced catalytic activity of clay minerals may be the presence in areas of degradation of the basement polycyclic organic compounds in a larger amount than the organic substance diffused [3].

Theory and/or Method

To test the possibility of conversion to hydrocarbons geofluids under catalytic influence of thin structurally deformed clay were conducted modeling experiments. As a starting reagent used methane as the main organic component of underground fluids with a very large migration ability and physical and chemical stability. Natural clays were used for the preparation of reagents and catalytic properties. They were subjected to special chemical and mechanical action using an ultrasonic apparatus and dilute hydrochloric acid, and then converted into a nanostructure. The simulation process is carried out in an autoclave at a metal temperature of 300°C and a pressure of 15 atm for 8 hours -100.

Examples

The results showed that a new gas phase appears in the reaction space. It consists of inorganic compounds and mixtures of hydrocarbons (ethane - up to 70%, ethylene - 15%, propane – 10% and propylene - less than 5% (Table). The total yield of hydrocarbons is not exceeded 1%.
The reliability of the nature of the obtained unsaturated hydrocarbon compounds was confirmed by the qualitative reaction by Wagner bleaching solution of potassium permanganate in a weakly alkaline medium by gaseous reaction products.

$$3RCH=CHR_1 + 2KMnO_4 + 4HO_2 \longrightarrow 3RCH(OH)-CHR_1(OH) + 2MnO_4 + 2KOH,$$

where R, R_1 = H or CH_3

As well as passing the gas-phase reaction mixture through a solution of sulfuric acid (sulfation reaction) followed by chromatographic identification of components in the output.

$$H_2C=CH_2 + H_2SO_4 \longrightarrow H_2C - C(H)OSO_3H$$

The amount of water used in the process under study, as follows from the experimental data (Table.) Has no significant effect on the yield of new compounds. Perhaps, in this case, the limiting step of the mechanism for converting methane in this case is another factor, and not the quantity of steam during both the steam reforming [4].

To isolate the liquid-phase products of such samples they were treated by polinar solvent consisting of chloroform, alcohol and benzene. The study of the extracts was carried out with the assistance of HPLC method, which is found in the spectra of peaks of 32 new organic compounds. Through the use of internal standards are well established that 8 of them are polycyclic aromatic compounds: naphthalene, flouren, anthracene, phenanthrene, pyrene, chrysene, flouranten, acenaphthylene. The amount of each averaged 10^{-5}% wt., the total amount did not exceed 10^{-3}% wt. It should be noted that the same compounds were found in the basement rocks of the South Tatar arch [3].

Table. The composition of the gaseous products of the experiment (duration - 28 hours at 300ºC)

Experimental conditions	Content of the gaseous products, % weight.				
	CH_4	ΣC_2+C_3	H_2	CO	CO_2
H_2O - 5,0*	63,54	0,2	25,5	0,04	5,57
H_2O - 7,0*	67,22	0,23	19,62	0,08	4,59
H_2O - 10,0*	68,27	0,37	13,56	0,04	6,06
H_2O - 14,0*	68,43	0,13	17,67	0,06	5,36

* The percentage of water relative to methane

Taking into account all the identified products of synthesis, we can assume the following scheme for the hydrocarbons formation. At the first stage is the transformation of methane by steam reforming type with the formation of synthesis gas, which in these conditions can be easily transformed into hydrocarbons of various structures as follows

The hydrocarbons formation scheme

Steam reforming with the formation of synthesis gas

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (\Delta H = 226\ kJ)$$

further - cooperation on the type of the Fischer-Tropsch scheme

$$CO + 2H_2 \rightarrow (-CH_2-) + H_2O \qquad (\Delta H = -165\ kJ)$$

$$2CO + H_2 \rightarrow (-CH_2-) + CO_2 \qquad (\Delta H = -204{,}7\ kJ)$$

and the conversion

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (\Delta H = -39{,}8\ kJ)$$

$$3CO + H_2O \rightarrow (-CH_2-) + 2CO_2 \qquad (\Delta H = -244{,}5\ kJ)$$

$$CO_2 + 3H_2 \rightarrow (-CH_2-) + 2H_2O \qquad (\Delta H = -125{,}2\ kJ)$$

$$CH_4 \longrightarrow C_2H_6 \rightarrow C_2H_4, CnHm \longrightarrow PAH \ldots \rightarrow Csol$$

where $n \geq 3$, PAH - polycyclic aromatic hydrocarbons

Conclusions

Thus, presence in the resulting reaction mixture of hydrocarbons of different nature suggests the possibility of transformation geofluids catalyst, in particular methane in natural conditions. The implementation of such thermodynamically allowed process can occur in areas of destruction of the basement and in the sediment in cases of various types of tectonic shifts and temperature emanations. Thus obtained by the catalytic process hydrocarbons are able to fill the accumulation of oil, forming a wave of re-entry. An example of such a process may be the so-called "anomalous" high-yield wells Romashkinskoye field [5]. In this case, in terms of higher biomarkers, such as hopanes and steranes, there is an increase catagenetic maturity of crude oil produced in comparison with the usual [6], but the isotopic composition remains unchanged [7].

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