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EXPERIMENTAL MODEL OF THE CATALYTIC TRANSFORMATION OF DEEP FLUIDS IN NATURAL CONDITIONS

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Based on the results of experimental simulation it was shows that in zones of destruction of the crystalline base the is a feasibility of conversion of enriched methane geofluid into complex hydrocarbons of different nature under the influence of the catalytic activity of fine structural changes of clay minerals of these zones.
Keywords: geofluid, catalytic, clay minerals

The presence of underground fluids enriched in methane of various origins in the Earth's crust is beyond doubt. Molecule of this hydrocarbon having small geometrical dimensions and low chemical activity are able to move in place for quite long distances and accumulate in the traps of various types. In suitable conditions, methane, as pointed out by N.D. Zelinsky, can be a "source of all the hydrocarbons that make up the oil". But the gaseous alkanes are known to show their reactivity only at temperatures above 1000ºC, which is unlikely to achieve at commercial development of the depths. However, in the presence of catalysts their transformation can take place under milder conditions.

In nature there are known minerals that have catalytic properties. They are oxides, metal sulfides, etc. However, the most common are the fine clay mineral associations, representing more than 60% of the sedimentary rocks of the crust. Structurally, they represent a heterogeneous layer of continuous two-dimensional grid consisting of coincident with each other silica tetrahedra (30-70%) and aluminum oxide octahedron (10-40%). It's combinations result in multiple layered clay minerals - kaolinite, montmorillonite, mica, chlorite, etc. They also include the water molecules in an amount of 5-10%.

Destruction zones are revealed in the basement underlying the sedimentary rocks of the South Tatar arch through the study of core materials, which found out a complex set of crushed rock in a mass of clay minerals. By using a scanning electron microscope a presence in those areas of agglomerates of clay particles in the form of nano-sized cylinders, spheres, hemispheres was recorded. The presence of structurally modified clays in the foundation areas of destructions may be associated with severe thermobaric conditions of their formation. Such conditions contribute to a partial removal of water molecules from the interlayer spaces of the crystal lattices of clay minerals, and as a result lead to their deformation (Fig.).

Change of the structural characteristics of clay minerals involves an increase of energetically no compensated active sites on their surfaces. Additional formation of reactive charged particles is due to the fact that after partial dehydration the number of mobile protons of the hydroxyl groups of metal oxides (Brensted centers), and coordinatively unsaturated metal ions (Lewis centers) increases. In general, it can significantly enhance the catalytic properties of structurally modified clay minerals.

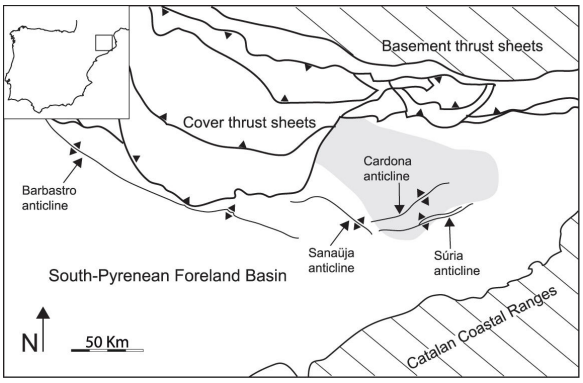


Fig.1. The scheme of structural transformation of clay minerals as a result of partial removal of interlayer water molecules.

Organic compounds in excess of polycyclic nature of dispersed organic matter quantity can present the development of the increased catalytic properties of clay minerals in destruction zones of basement. The presence of organic compounds at such depths is usually connected with an immigrant character.

However, the movement of substances of such a complex structure on the fracture-cavernous reservoirs of dense basement rocks is unlikely. More possible that they are products of conversion of other compounds capable of more migration and methane that catalytically reacts to transformation under the influence of structurally modified clays.

To test this hypothesis, some experiments were performed - conditions of destruction zones were simulated. For this purpose, the methane in the presence of clay samples in high-pressure metal reactor heated to 300ºC and pressures up to 8 atm for 8 to 100 h. The most active reactionary ability catalytic mixes is observed at temperatures about 250^0C. Further temperature increase results a destruction of tetrahedral grids smektite's structure and appearance of additional quantities of fine-dispersed quartz. Structural defects of natural clay, resulting to tubular and fullerene-similar nanostructures appearance, promote the increase of it's catalytic activity up to a level, sufficient for initiation of transformation of methane molecules.

The reason for this is the feasibility of catalytic processes for small-sized molecules of fluids in the interlayer space of weakly clay lattices, whose dimensions range from one to several nanometers. Increasing the frequency of interaction of "guest" molecules with the walls of the layer of "owner" molecules - the oxygen atoms of the clay matrix in such a kind of "nanoreactors" will lead to a loosening of the C-H bond. Thus activation of the conversion process of fluids requires energy expenditure comparable to the thermobaric conditions of terrestrial rocks.

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.

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.

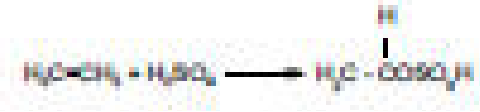


Table. The composition of the gaseous products of the experiment (duration - 28 hours at 300ºC)

Con-ditions	Content of the gaseous products, % weight				
	CH_4	ΣC_2+C_3	H_2	CO	CO_2
H_2O - 5,0*	83,54	0,20	25,50	0,04	5,57
H_2O - 7,0*	87,22	0,25	19,62	0,06	4,59
H_2O - 10,0*	88,27	0,37	13,56	0,04	8,06
H_2O - 14,0*	88,43	0,15	17,67	0,06	5,36

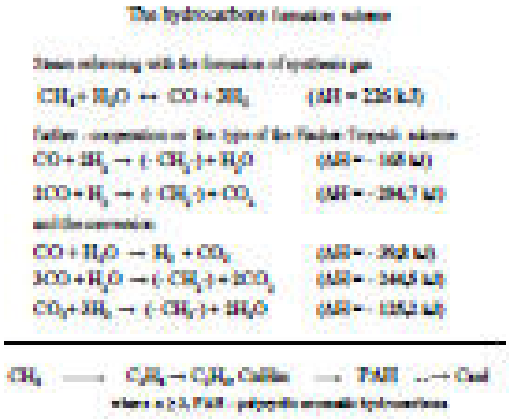
*The percentage of water relative to methane

In this process carried out by the type of steam reforming a significant effect on the yield of the products may have the amount of used water. To test this hypothesis, experiments were performed with the increased water content. However, significant changes in the release of new compounds were not detected (Table). Probably, in this case the limiting stage of the mechanism of conversion of methane is another factor, but not a sufficient number of steam.

Clay minerals samples used in the experiments as the catalyst. 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 [5].

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:



Thus, experiments show that the enriched with methane underground fluids in destruction zones under the catalytic action of structurally modified clay minerals of such areas are transformed into complex hydrocarbons of different nature and, consequently, different migration abilities. This leads to the fact that the mobile part is moved to higher horizons of the Earth's crust, and fixed part remains in place of formation in the destruction zones

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