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Catalytic Conversion of Oil in Model and Natural Reservoir Rocks

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Abstract: The catalytic activity of metal oxides in the processes of low- and high-temperature oxidation (LTO and HTO, respectively) of oil was studied on model systems consisting of oil-saturated quartz sand with additives of Al_2O_3, Cr_2O_3 and MgO using thermal analysis methods. The used additives were shown to shift the LTO and HTO processes to the low-temperature region. The catalytic activity of a natural reservoir carbonate rock without and with water was studied. This study established that at room temperature in dry carbonate rock, the oil components undergo dealkylation and polycondensation of aromatic fragments for a week. In the presence of water, the polycondensation processes are suppressed, and the cracking of resin and asphaltene occurs. The cracking reactions lead to a decrease in the content of heteroatoms in resins and asphaltenes.

Keywords: natural catalysts; low temperature conversion; in situ oil conversion; resin; asphaltene

1. Introduction

At present, the portion of hard-to-recover reserves, which include high-viscosity oil, bitumen and oil in carbonate reservoirs, increases in global oil production. Traditional recovery methods used in the development of these fields are ineffective due to the high viscosity of oil (more than 35 MPa·s) and low reservoir permeability [1]. This problem can be solved by developing more advanced technologies that imply a complex thermal effect on oil reservoirs, including the use of catalysts. These technologies include catalytic upgrading process in situ (CAPRI), in situ upgrading technology (ISUT) and in situ heavy oil aquathermolysis [2–6]. The thermal effect is used to reduce the viscosity and density, and catalysts (nanocatalysts, Co or Ni Mo/Al_2O_3 catalysts) are used to improve the quality of oil due to the in situ cracking of hydrocarbons [7,8]. The injection of hydrogen or water facilitates hydroprocessing reactions, which makes it possible to obtain higher quality oil (in particular, with a lower sulfur content) and reduce coke formation in the reservoir [2,6]. The authors of [9] proposed to carry out catalytic processes of hydrocarbon conversion in the reservoir by activating natural catalysts (Fe_2O_3, MnO_2, Cr_2O_3, etc.) in oil-field waters.

The main factors that affect the conversion of oil in the reservoir are the oil composition, temperature, time, pressure and the presence of water and minerals. In the process of oil conversion, the amount of thermally stable saturated hydrocarbons increases. Asphaltenes are the most stable of the high-molecular oil components [10]. It was shown [11] that at low temperatures (temperature < 50 °C), the composition of oils with a high content of saturated hydrocarbons does not change, in contrast to oils with a high content of aromatic hydrocarbons.

Metals that are part of such natural rocks such as feldspar, quartz and clays exhibit catalytic activity in the processes of in situ oil conversion [12]. The catalytic activity of rocks is mainly due to the presence of a clay, which significantly accelerates the reactions of cracking, isomerization and dealkylation and the reactions of hydrogen redistribution by the donor–acceptor mechanism. However, a number of works also note the catalytic activity of carbonate rocks. Thus, in [13], a significant effect of carbonates on the cracking of oil hydrocarbons was shown. The thermal effect on heavy oil in a carbonate rock leads to the cracking of resin and asphaltene. As a result, the mobility and quality of heavy oils increase. However, as the temperature increases, the intensity of the polycondensation reactions of oil hydrocarbons increases significantly, and coke formation occurs [14].

There are a lot of data on the catalytic activity of rocks during oil conversion at temperatures above 200 °C [2,15]. However, two facts should be noted. Firstly, the differences in the catalytic action of natural minerals decrease at high temperatures [16]. Secondly, the processes of oil conversion at geological conditions (duration, temperature < 150 °C, high ratio of rock/organic matter) and at high temperatures (300–400 °C) are the same [10,11].

There are two goals in this work as follows: (1) to evaluate the influence of metal oxides on the processes of thermal oxidative degradation of the oil in model rock; (2) to study the process of oil and high-molecular oil component conversion at low temperatures (about 25 °C) in natural carbonate rock.

2. Materials and Methods

2.1. Materials

Model and natural oil-saturated rocks were used in this study. The heavy oil taken from the Ashalchinsky field was used for the preparation of the model and natural oil-saturated rocks. The oil density at 20 °C is 0.965 g/cm^3; the viscosity at 20 °C is 1140 mm^2/s.

Quartz sand (100% quartz, particle size $\leq$ 0.4 mm) and quartz sand with the addition of 1% wt. various metal oxides (Al_2O_3, Cr_2O_3, MgO) and salt (Na_3PO_4) were used for the preparation of model oil-saturated rocks.

Carbonate rock (38% wt. particles with size > 0.1 mm, 53%wt. particles with size 0.1–0.2 mm and 9%wt. particles with size 0.2–0.5 mm) was used for the preparation of natural oil-saturated rocks. The used carbonate rock contains calcite (39.9%) and aragonite (37.0%), as well as muscovite (10.9%), montmorillonite (6.2%), quartz (3.1%), clinochlor (2.1%) and dolomite (0.8%). For the preparation of model oil-saturated rocks, "dry" (without water) or "wet" (rock/water ratio = 4:1) carbonate rocks were used.

The oil-saturated rocks were prepared by mechanical mixing of the rock with the oil in a ratio of 3:1. Then, the prepared rock was kept at a temperature of 25 °C for a week. Then, oil was extracted from the natural oil-saturated rocks and the extracted oil composition was determined.

2.2. Thermal Analysis

Thermal analysis of model oil-saturated rocks was carried out on a derivatograph Q—1500D (Hungary) in the temperature range of 20–1000 °C with a heating rate of 10 $^\circ$/min. The stationary atmosphere was air. Aluminum oxide was used as an inert substance in the reference cell. A platinum crucible was used in the experiments. The weight of the oil-saturated rock was 300 mg. Mass losses, temperature intervals and maximum temperatures of thermal effects were determined. The experimental error on the temperature ranges, and the maximum temperature is 2–4 °C.

2.3. SARA Analysis

The contents of saturates, aromatics, resin and asphaltene (SARA composition) were determined using the method described below. Asphaltene was isolated directly from the oil-saturated rock via precipitation with a 40-fold excess of n-heptane relative to oil (ASTM D6560-17 [17]). The precipitate was extracted in the Soxhlet apparatus first with n-heptane to remove the coprecipitated maltene components and then with benzene to extract

asphaltenes. The separation of the maltene into saturates, aromatics and resin was carried out using preparative liquid chromatography (GOST11244-2018 [18]). A glass column was used. The length was 55 cm, and the diameter was 20 mm. Silica gel of the ASK brand was used as an adsorbent. Maltenes were first separated into saturated + aromatic, nonpolar and polar resins using hexane, benzene and a mixture of benzene and isopropyl alcohol, respectively. The solvent was removed from eluents containing petroleum components via distillation. Petroleum components were dried to a constant weight. Then, a mixture of saturates and aromatics was also separated on a glass chromatographic column. The solvents were hexane and benzene. The eluent was taken in 20 mL increments, the solvent was removed, fractions were dried to a constant weight and the refractive index of the fractions was determined. Fractions with a refractive index of less than 1.49 were classified as saturates, and those with a refractive index of more than 1.49 were classified as aromatics. The discrepancy between two parallel experiments does not exceed 1–2% wt.

2.4. CHNS Analysis

Elemental analysis of asphaltene and resin was carried out on a EuroEA3028-HT-OM CHNS analyzer via Eurovector SpA (Milan, Italy). Samples were weighed on microweights of Sartorius CP2P (Goettingen, Germany) in tin capsules. Callidus 4.1 software was used to carry out quantitative measurements and evaluate the data obtained. Sulfanilamide was used for calibration. By subtracting the contents of C, H, N and S from 100%, the total contents of oxygen and metals were estimated. The elements (carbon, hydrogen, nitrogen and sulfur) were analyzed twice. The discrepancy between two parallel experiments does not exceed 1% wt.

2.5. IR Spectroscopy

IR spectra were recorded on a Tensor 27 "Bruker" spectrometer (Ettlingen, Germany) in KBr tablets in the wavelength range from 4000 to 400 cm^{-1} (optical resolution 4 cm^{-1}). Number of scans was 64. The detector was DTGS Mir. Typical IR spectrum of high molecular oil components is presented in Supplementary Materials. The spectra were processed via the OPUS 7/2012 program using a common baseline for a group of bands in the 2000–400 cm^{-1} region; the spectrum was normalized to the 1470 cm^{-1} band. The intensity of the main absorption bands (1700 cm^{-1}, 1600 cm^{-1}, 1380 cm^{-1}, 1030 cm^{-1} and 720 cm^{-1}) characterizing the structure of high-molecular oil components [19] was determined. The spectral coefficients A, R, O1 and O2 were calculated as follows:

$$A = \frac{\text{optical density at 720 } cm^{-1}}{\text{optical density at 1600 } cm^{-1}}, \tag{1}$$

$$R = \frac{\text{optical density at 1380 } cm^{-1}}{\text{optical density at 1600 } cm^{-1}}, \tag{2}$$

$$O1 = \frac{\text{optical density at 1700 } cm^{-1}}{\text{optical density at 1600 } cm^{-1}}, \tag{3}$$

$$O2 = \frac{\text{optical density at 1030 } cm^{-1}}{\text{optical density at 1600 } cm^{-1}}. \tag{4}$$

IR spectra were taken three times, and the average values were calculated. The discrepancy between the values of the spectral coefficients did not exceed 0.1.

2.6. EPR Spectroscopy

EPR spectra of asphaltene were taken on an ELEXSYS E500 spectrometer (Bruker, Mannheim, Germany). Two types of signals were recorded—a single symmetric signal of stable free radicals (SFRs) (g = 2.003) and a multicomponent hyperfine structure corresponding to VO^{2+} ions in vanadyl complexes (VP). The obtained values of the intensities

of the corresponding lines in the EPR spectra were normalized by the mass of the used sample, obtaining values in relative units that characterize, respectively, the contents of SFR and VP in asphaltene. The relative measurement error did not exceed 5%

2.7. Gas–Liquid Chromatography

The composition of alkanes was studied via gas–liquid chromatography (GLC). The analysis was carried out on a Chromatek Crystal 2000 M gas chromatograph with a flame ionization detector and temperature programming from ambient temperature to 400 °C. The heat rate was 3 °C/min. The J&W Scientific DB-1 column was used. The length was 15 m, and the diameter was 0.32 mm. Samples were dissolved in CCl_4 at a ratio of 1:20. The distribution of normal and isoprenoid alkanes was calculated using the method of internal normalization. The relative measurement error did not exceed 5%.

3. Results

3.1. Evaluation of the Catalytic Activity of Metal Oxides

In order to evaluate the catalytic activity of metal oxides (Al_2O_3, Cr_2O_3 and MgO) in reservoir rock, the processes of oil conversion in the model oil-saturated rocks were investigated via thermal analysis in the air atmosphere. Such metal oxides simulate impurities in natural minerals. It is well known, for example, that Al_2O_3 is a part of clay minerals, Cr_2O_3 is included in muscovite and MgO is included in dolomite. Also, the possibility of promoting the catalytic properties of metal oxides via Na_3PO_4 was evaluated. Na_3PO_4 is the optimal promoter in the oxidative processes of low-molecular alkane production [20]. So, it was chosen as the promoter in our study.

The TG, DTG and DTA curves of oil-saturated quartz sand, as well as oil-saturated quartz sand with additives of metal oxides, are the same and show three main stages of thermal oxidative degradation of oil [21]. The first stage (250–380 °C) is low-temperature oxidation (LTO), where evaporation and thermal oxidation of light and medium fractions of oil occur. At the second stage (380–500 °C), the processes of oxidation and destruction of peripheral substituents in polycyclic aromatic structures and the polycondensation of organic compounds take place. These processes have an endothermic effect. The third stage (500–610 °C) is the high-temperature oxidation (HTO) of polycyclic aromatic structures in oil. A typical curve of a model oil-saturated rock is given in Figure 1. For the studied model systems, mass losses at different stages of thermo-oxidative destruction, temperature intervals of three stages as well as the maximum temperatures of the effects of LTO (T_{max1}) and HTO (T_{max2}) were determined (Table 1).
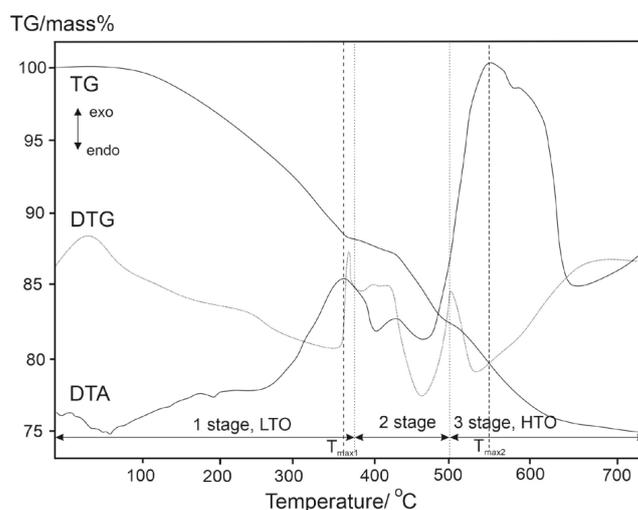
Figure 1. DTA, TG and DTG curves of oil-saturated quartz sand without additives.

Table 1. The data of thermal analysis of model oil-saturated rocks.

	Sample	Temperature, °C			T_{max1}, °C	T_{max2}, °C
		Stage 1, LTO	**Stage 2**	**Stage 3, HTO**		
1.	Quartz sand	268–387	387–501	501–636	354	549
2.	+1% Cr_2O_3	250–373	373–491	491–595	341	539
3.	+1% MgO	255–376	376–493	493–607	356	543
4.	+1% Al_2O_3	263–380	380–497	497–625	348	544
5.	+1% Al_2O_3 + Na_3PO_4	256–378	378–497	497–609	348	537
		Mass losses, % wt.				
1.	Quartz sand	12	6	7		
2.	+1% Cr_2O_3	13	7	6		
3.	+1% MgO	12	6	7		
4.	+1% Al_2O_3	13	6	7		
5.	+1% Al_2O_3 + Na_3PO_4	13	6	6		

The introduction of additives does not lead to a significant change in the mass loss of oil at the different stages of thermal oxidative degradation. The mass losses are −12–13% wt. at the LTO, and 6–7% wt. at the second stage and at the HTO. At the same time, there is a change in the temperature intervals (Table 1) for the model systems with metal oxides. The introduction of metal oxides into quartz sand leads to a shift in the stages of thermal oxidative degradation towards lower temperatures. The temperatures of the maxima of the LTO are shifted towards lower temperatures by 13 and 6 °C when Al_2O_3 and Cr_2O_3 are added to the sand. The addition of Na_3PO_4 to Al_2O_3 leads to a decrease in the temperature of the beginning of the LTO (from 263 to 256 °C), but the temperature of the maximum (T_{max1}) does not change.

In the model rocks with metal oxides, the maximum of the HTO effect and the temperature of the end of the thermal oxidative degradation are also shifted towards lower temperatures by 5–12 °C and 11–41 °C, respectively. The shifts of these parameters are greater in the model rocks with Cr_2O_3 and Al_2O_3 promoted by Na_3PO_4.

Thus, the shift of the temperature intervals of thermal oxidative degradation towards lower temperatures shows that metal oxides accelerate the processes of the LTO and HTO of oil. The most active components in the process of oxidation are Cr_2O_3 and Al_2O_3, which are present in natural minerals such as muscovite and montmorillonite. The possibility of promoting the activity of natural catalysts by salt additives, particularly Na_3PO_4, is shown.

3.2. The Change in SARA Composition of Oil in Natural Rock at Low Temperature

The process of the low-temperature catalytic conversion of oil in natural carbonate rock was modeled at 25 °C. It should be noted that in the used carbonate rock, there are minerals (montmorillonite 6% wt., muscovite 11% wt. and dolomite 1% wt.), which contain Al_2O_3 and Cr_2O_3. These impurities, according to the thermal analysis, exhibit catalytic activity in the LTO process. The content of saturates, aromatics, resin and asphaltene was determined in the oil extracted from dry (oil ex dry) and wet (oil ex wet) carbonate rocks. The data are given in Table 2.

Table 2. SARA composition of initial oil and oil extracted from carbonate rocks.

Sample	Content, % wt.				
	Saturates	**Aromatics**	**Nonpolar Resin**	**Polar Resin**	**Asphaltene**
Initial oil	24.5	46.4	13.0	9.3	6.8
Oil ex dry	24.6	36.9	21.8	9.5	7.2
Oil ex wet	27.3	47.2	16.2	4.6	4.7

The SARA composition of the oil extracted from the dry and wet carbonate rocks differs from the that of the initial oil. In the oil extracted from the "dry" carbonate rock, the contents of saturates, asphaltene and polar resin practically do not change. But the contents of nonpolar resin increases (from 10 to 22% wt.) and aromatics decreases (from 46 to 37% wt.) significantly. In the oil extracted from the wet carbonate rock, the contents of polar resin (from 9 to 5% wt.) and asphaltene (from 7 to 5% wt.) decrease, and the contents of nonpolar resin (from 13 to 16% wt.), saturates (from 24 to 26% wt.) and aromatics (from 46 to 48% wt.) increase. It should be noted that the SARA composition of the oil in the dry carbonate rock shows greater changes than in the wet carbonate rock.

The saturates were studied via gas–liquid chromatography (Figure 2). As seen in Figure 2, the initial oil contains isoprenoid alkanes C14-C20 and n-alkanes C12 and C13 only. In the oil extracted from the carbonate rock, the contents of n-alkanes C12 and C13 increase, and the n-alkanes that are not in the initial oil appear. The alkanes from C11 to C16 are found in the oil extracted from the dry rock, and the n-alkanes from C10 to C20 are found in the oil extracted from the wet rock. The composition of isoprenoid alkanes changes slightly. Chromatogram of saturates are presented in Supplementary Materials.
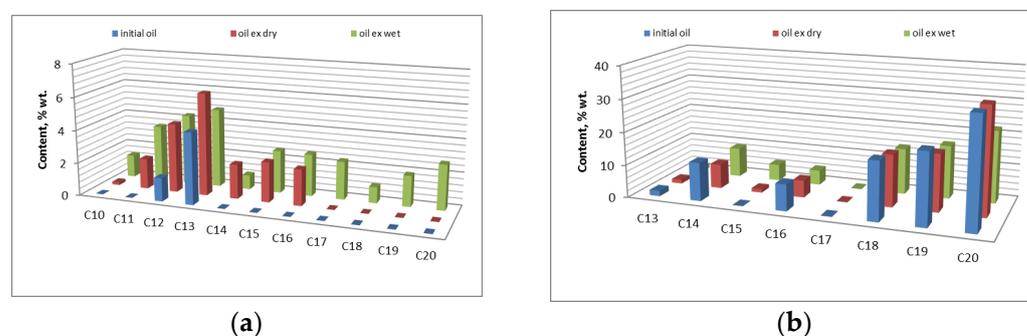
Figure 2. Distribution of normal (**a**) and isoprenoid (**b**) alkanes.

Thus, in the dry carbonate rock, the side substituents in the aromatic hydrocarbons are detached. Then, a polycondensation of the obtained aromatic fragments into higher molecular components, namely nonpolar resins, occurs. In the wet carbonate rock, the detachment of side substituents in the polar resins and asphaltenes and the cracking of naphthenic structures occur, while the polycondensation processes slow down. Thus, water intensifies the catalytic cracking of high-molecular components (resin and asphaltene) as with the high-temperature conversion [22,23].

3.3. Changes in the Composition of High-Molecular Oil Components

The composition of high-molecular oil components (resin and asphaltene) was studied using the method of elemental analysis (Table 3). The C/H index in the high-molecular components extracted from the wet rock is lower than in the initial oil and the oil extracted from the dry rock. This shows that the portion of saturated structure increases, and the portion of aromatic structure decreases in resin and asphaltene. It can be assumed that water acts as a hydrogen donor, suppressing the polycondensation reactions of aromatic hydrocarbons. Also, in the high-molecular components extracted from the wet rock, the sulfur content decreases from 11 to 8–9% in polar and nonpolar resins. The content of oxygen and metals significantly decreases (to 0.1–0.2%) in polar and nonpolar resins and asphaltene. This indicates that the reaction of desulfurization and oxygen and metal removal reactions occurs in high-molecular components when there is water in the rock. The processes occurring in the wet rock are similar to those occurring during hydrotreating.

Table 3. Elemental composition of high-molecular oil components.

Parameter	Sample	Content, % wt.		
		Nonpolar Resin	Polar Resin	Asphaltene
C	Initial oil	79.2	77.0	78.9
	Oil ex dry	81.1	78.7	76.0
	Oil ex wet	81.4	81.1	81.4
H	Initial oil	5.7	5.1	5.9
	Oil ex dry	5.7	5.3	5.7
	Oil ex wet	9.3	9.2	8.0
N	Initial oil	0.4	0.8	1.2
	Oil ex dry	0.3	0.8	0.7
	Oil ex wet	0.8	0.8	1.3
S	Initial oil	10.6	10.9	9.5
	Oil ex dry	11.2	11.4	11.8
	Oil ex wet	7.9	8.8	9.2
O, Me	Initial oil	4.1	6.2	4.5
	Oil ex dry	1.7	3.8	5.8
	Oil ex wet	0.1	0.1	0.2
C/H	Initial oil	13.9	15.1	13.4
	Oil ex dry	14.2	14.9	13.4
	Oil ex wet	8.8	8.8	10.2

Changes in the compositions of resin and asphaltene under carbonate rock were detected using the IR spectroscopy method (Table 4). There are groups of bands corresponding to the valence vibrations of the carbonyl group in carboxylic acids and ketones (1700 cm^{-1}), the skeletal vibrations of aromatic C=C bonds (1600 cm^{-1}), the deformation vibrations of the methyl group (1460 and 1380 cm^{-1}), the valence vibrations of the sulfoxide group (1030 cm^{-1}) and the rocking vibrations of the methylene group (C > 4) (720 cm^{-1}) on the IR spectra of the high-molecular oil components [24]. The spectral coefficients A, R, O1 and O2 show the quantities of long-chain methylene (A), methyl (R), carboxyl (O1) and sulfoxide (O2) structures relative to the aromatic ones.

Table 4. Spectral coefficients of high-molecular oil components.

Spectral Coefficient	Sample	Values of Spectral Coefficients		
		Nonpolar Resin	Polar Resin	Asphaltene
A	Initial oil	0.7	0.5	0.4
	Oil ex dry	0.4	0.4	0.2
	Oil ex wet	0.4	0.4	0.2
R	Initial oil	2.7	2.0	1.6
	Oil ex dry	2.3	2.1	1.6
	Oil ex wet	1.9	2.3	1.7
O1	Initial oil	0.6	0.1	0.3
	Oil ex dry	0.5	1.0	0.4
	Oil ex wet	0.5	1.3	0.2
O2	Initial oil	1.0	1.4	0.7
	Oil ex dry	1.1	1.6	1.3
	Oil ex wet	0.9	2.2	1.3

For the oil extracted from the dry carbonate rock, the structure of the high-molecular component does not change much. The spectral coefficient A decreases from 0.5–0.7 to 0.4 in resin and from 0.4 to 0.2 in asphaltene. Thus, the portion of aliphatic fragments

to aromatic fragments decreases in them. This is due to the detachment of side aliphatic substituents in condensed naphthenoaromatic structures.

In asphaltene, the content of sulfoxide groups (O2) (Table 4) and the sulfur content (Table 3) also increase. Thus, the oxidation of the S atom occurs only in the asphaltene of the oil extracted from the dry carbonate rock. The formation of sulfonic groups is possible with an excess of an oxidizing agent [25].

In the polar resin and asphaltene from the wet carbonate rock, the rupture of bridging sulfur-containing bonds in the molecule may occur. In this case, the sulfur content decreases (Table 3), and the relative number of sulfoxide groups increases. This is in good agreement with the previously made assumption that water can act as a hydrogen donor, initiating the hydrodesulfurization process. In this case, the conversion process of high-molecular components is similar to the desulfurization processes occurring at aquathermolysis (250 °C) [26].

Using EPR spectroscopy (Table 5), it is shown that the contact of the oil with carbonate rock does not lead to a change in the content of stable free radicals (SFRs) and vanadylporphyrin complexes (VP) in the asphaltene. The slightly reduced contents of SFR and VP in the asphaltene isolated from the oil extracted from the dry rock are due to the co-deposition of fine carbonate particles with asphaltenes. The fine particles of carbonate rock dissolve in water [27], and it prevents their co-deposition with asphaltenes. All of the studied asphaltenes have the same SFR/VP ratio. This indicates that the catalytic action of carbonate rock does not affect the condensed naphthenoaromatic structures in which SFR and VP are localized, unlike high-temperature processes in which demetalization begins at temperatures above 300 °C [28].

Table 5. EPR spectroscopy data of asphaltene.

Sample	Content, c.u.		SFR/VP
	SFR	VP	
Initial oil	1.88	1.26	1.5
Oil ex dry	1.60	0.97	1.6
Oil ex wet	1.89	1.24	1.5

Thus, the activity of natural carbonate rocks in the processes of low-temperature (25 °C) conversion of petroleum components was proven. It was recorded that the reactions of a detachment of side substituents in aromatic hydrocarbons and high-molecular components occur. In asphaltene, oxidation reactions of the S atom are possible. It was shown that even at low temperatures, water can act as a hydrogen donor, suppressing polycondensation reactions and facilitating the reactions of the removal of heteroatoms (S, O and Me).

The most probable low-temperature conversion reactions for the averaged molecules of oil components [29] are given below. The assumption was made that the conversion of oil in dry carbonate rock proceeds according to Equations (5) and (6), and the conversion of oil in wet carbonate rock proceeds according to Equations (7) and (8).

(5)

(6)

$$\text{(7)}$$

$$+ RH + R^IH + R^{II}H + R^{III}H + R^{IIII}H$$

$$\text{(8)}$$
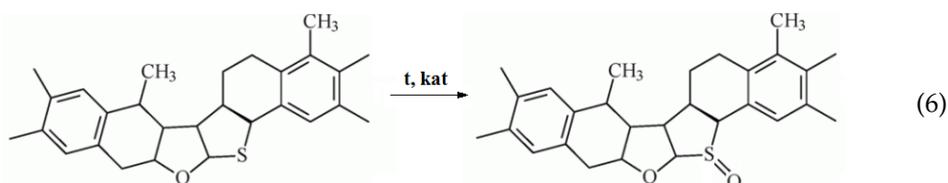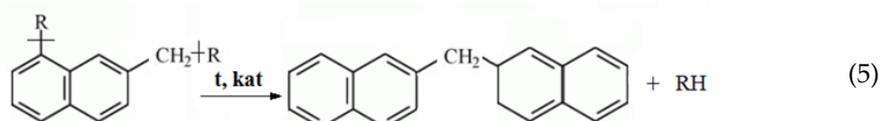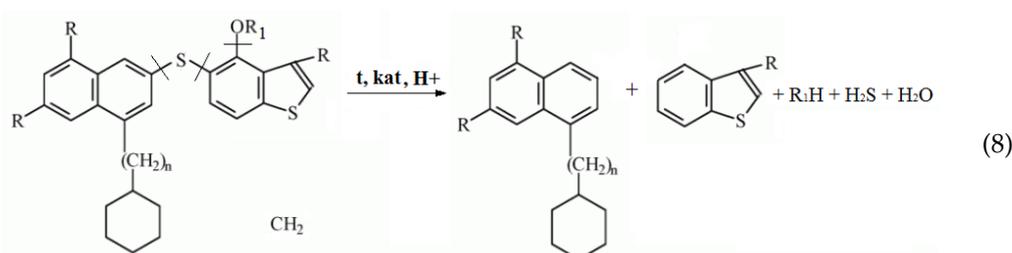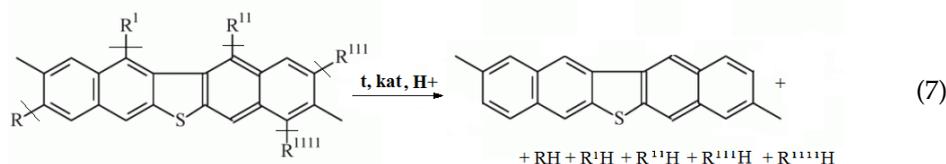
4. Conclusions

Thus, on the model oil-saturated rocks, the catalytic activity of metal oxides, particularly Cr_2O_3 and Al_2O_3, in the processes of low-temperature and high-temperature oxidation is shown. Also, the possibility of promoting the activity of natural catalysts by salt additives, particularly Na_3PO_4, is proven.

The possibility of a low-temperature conversion of oil in natural carbonate rock is shown. In dry (without water) carbonate rock, the reactions of a detachment of side substituents in low-molecular aromatic hydrocarbons and the polycondensation of aromatic fragments occur. As a result, the content of nonpolar resins in oil increases. The structure of high-molecular oil compounds does not undergo significant changes. In asphaltenes, the content of sulfoxide groups may increase due to the oxidation of the atom S.

In wet (with water) carbonate rock, reactions of detachment of side substituents occur mainly in high-molecular components (resin and asphaltene). Polycondensation reactions that occur intensively in dry carbonate rock are suppressed. At the same time, the number of structures saturated with hydrogen increases, and the sulfur and oxygen contents decrease in all high-molecular oil components.

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