

CATALYTIC AQUATHERMOLYSIS OF HIGH-VISCOSITY OIL USING IRON, COBALT, AND COPPER TALLATES

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The results of a study of the composition of active forms of the catalyst formed upon degradation of the precursor, based on the results of physical modeling of a sample of high-viscosity oil having high asphaltene and resin contents, are presented. Oil-soluble iron, cobalt, and copper tallates were used as the objects of the study. The composition of the separated powder of the active form of the catalyst was determined by X-ray diffraction analysis, and the catalyst particle size was determined by scanning electron microscopy. The SARA (saturate, aromatic, resin and asphaltene) analysis data revealed a marked decrease in high-molecular-weight oil components due to thermocatalytic cracking. The basic transformation mechanism is breakdown of the high-molecular-weight compounds along the sulfur-bearing bonds, as indicated by elemental CHNS (carbon, hydrogen, nitrogen and sulfur) analysis data. It is shown that the cobalt- and copper-based oil-soluble complexes turn are converted to sulfide forms and the iron-based complex is converted to the oxide form. According to the results of scanning electron microscopic analysis of the catalyst, the particle size is about 60 nm.

Keywords: *high-viscosity oil, catalyst, catalyst precursor, aquathermolysis, X-ray diffraction analysis, scanning electron microscopy.*

As a consequence of the increased worldwide demand for energy carriers and of the depleted reserves of traditional resources the development of nontraditional sources of hydrocarbons is attracting more and

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more attention. Heavy oils comprise about 25% of the hydrocarbon resources [1-3]. The extraction of this stock is complicated by a large number of problems connected with the large content of high-molecular-weight hydrocarbon and hetero-containing compounds, leading to low mobility under production conditions as well as transportation and processing [4, 5]. The special features of heavy oils require development of new effective extraction techniques. The extraction methods used for heavy oil include thermal, chemical, and microbiological methods etc. [6, 7], among which steam-heat treatment is the method most widely used to intensify the extraction of oil. Nevertheless this method does have drawbacks. It involves large expenditures and the formation of free radicals during rupture of bonds formed during thermolysis and can lead to polymerization with the formation of larger molecules [8-10].

The extraction of oil by catalytic aquathermolysis is a promising alternative method of steam-heat treatment [11-13]. Aquathermolysis is essentially a modified steam flooding process. A catalyst and additives (a hydrogen donor) are injected into the rock together with steam in order to reduce the temperature of the oil conversion process and to lower the viscosity irreversibility as a result of transformation of the high-molecular-weight components of the oil and increase of the proportion of light hydrocarbons [14, 15]. The catalytic agents can be divided into four categories: mineral; water-soluble catalysts; catalysts soluble in the organic phase; dispersed catalysts [16-18].

In recent years fruitful researches have been carried out on the aquathermolysis of heavy oil with the use of catalytic agents based on transition metals such as iron, nickel, copper, cobalt, zinc, and tungsten [19, 20]. To fully understand the mechanism of the catalytic process it is necessary to study the final form of the catalyst that is formed from the oil-soluble precursor under thermobaric conditions.

Apart from the composition the activity of the catalyst is determined by the size of the particles that are formed, and this depends on the method of introduction of the catalyst precursor. The efficiency of their action increases with increase of the degree of dispersion of the particles. Investigations of combined catalysts containing two or more different catalytically active metals are promising [21-24]. It is considered that the active form of the catalyst is formed under the reaction conditions both during pumping of the oil-soluble

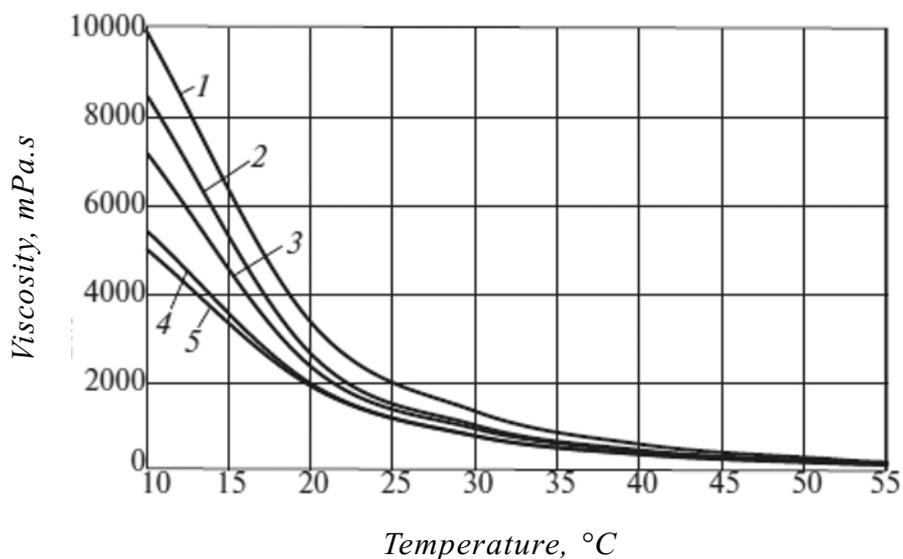


Fig. 1. Viscosity of oil samples before and after aquathermolysis: 1) original oil; 2) after aquathermolysis without catalyst; 3, 4, 5) after aquathermolysis with copper, iron, and cobalt tallate respectively.

precursors and during the use of metal oxides in the presence of sulfur-containing compounds. The catalytically active form here is most often the metal sulfides (hydrogenolysis catalysts) [25].

The present work presents the results from the use of oil-soluble metal sulfides based on cobalt and iron.

The sample used for the investigation was heavy high-viscosity oil from the Ashalchinsk deposit (Tatarstan Republic, Russia). The catalyst precursors were oil-soluble complexes of variable-valence metals (cobalt, iron, and copper) with carbonic acid.

The aquathermolysis process was modelled on a laboratory autoclave with agitation (volume 300 ml) from Parr Instruments (USA). The process was realized in nitrogen for 6 h at 300°C.

The viscosity of the crude oil and its transformation products was determined on a Fingilab Alpha L rotational viscosimeter. The group composition of the heavy oil samples before and after the transformations was determined by separation into saturate, aromatic hydrocarbon, resin, and asphaltene (SARA) fractions.

The CHNS elemental composition was determined on a Perkin Elmer 2400 Series II analyzer (USA).

The x-ray diffraction analysis (XDA) was conducted on a Shimadzu XRD-7000S automatic powder diffractometer. Scanning electron microscopic analysis was conducted on an AURIGA CrossBeam work station (Carl Zeiss, Germany).

Table 1

Sample	Content of hydrocarbon fraction, %				Decrease of high-molecular-weight fractions, %
	saturated	aromatic	resins	asphaltenes	
Original oil	26.83	39.02	28.78	5.37	-
Aquathermolysis products					
oil without catalyst	30.89	37.71	25.18	6.22	2.75
oil with catalyst based on					
copper	38.62	34.49	21.81	5.08	7.26
iron	37.83	39.05	18.32	4.80	11.03
cobalt	38.29	37.98	18.45	5.28	10.42

Table 2

Samples	Content of element, %				H/C
	C	H	N	S	
Original oil	81.35	8.78	1.51	6.08	1.30
Aquathermolysis products					
oil without catalyst	79.60	8.50	1.55	5.78	1.28
oil with catalyst based on					
copper	81.09	8.08	1.82	5.62	1.20
iron	77.52	6.85	1.87	5.27	1.06
cobalt	73.64	7.10	1.47	5.71	1.16

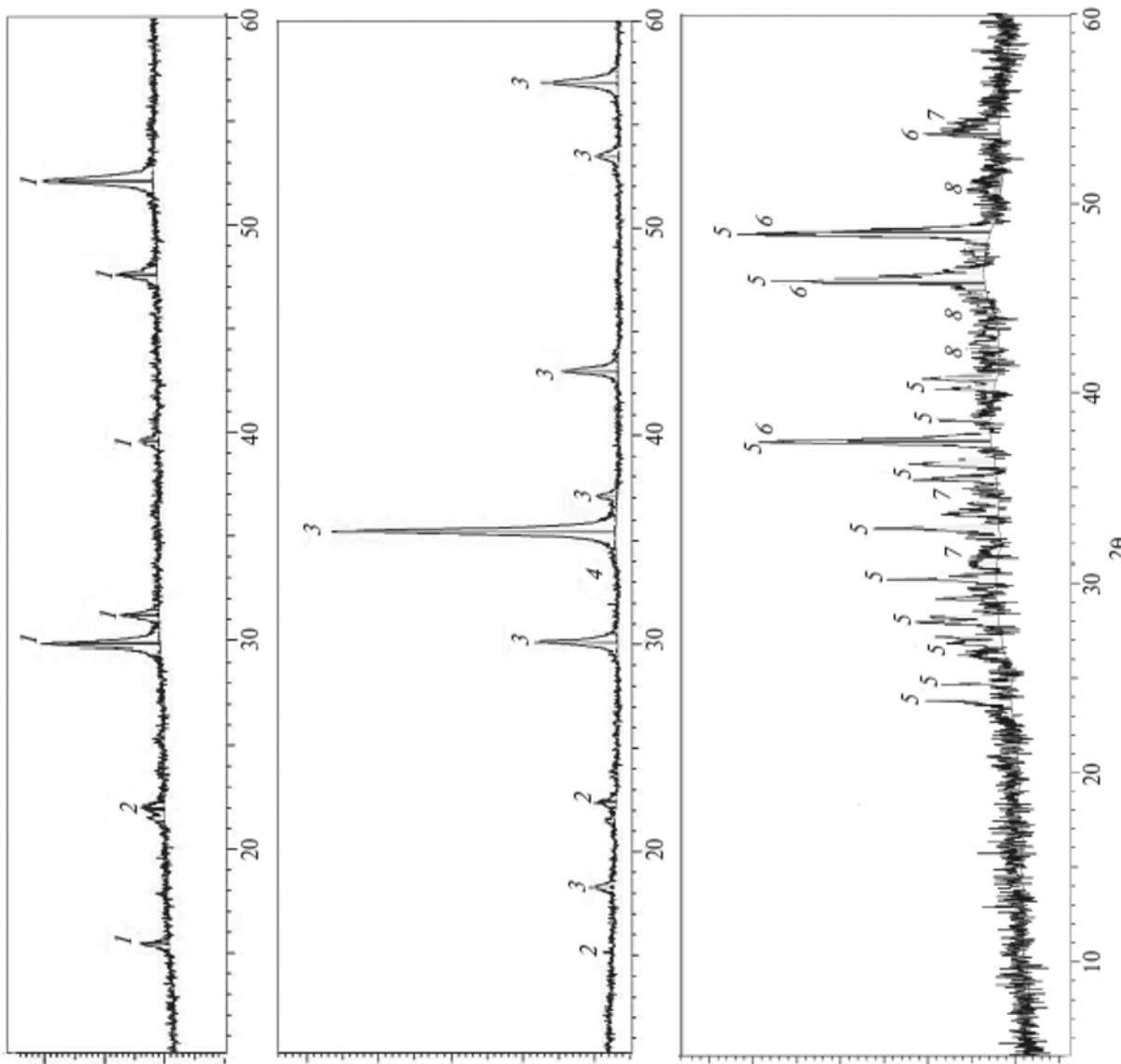


Fig. 2. X-Ray diffraction analysis of isolated catalyst particles based on cobalt (a), iron (b), and copper (c): 1) SiO_2 ; 2) Co_9S_8 ; 3) $\text{Fe}_{2,9}\text{O}_4$; 4) FeS_2 ; 5) Cu_2S ; 6) $(\text{Co}_7\text{Fe}_7\text{S}_{10})_{0.125}$; 7) Fe_3S_4 .

The results of the SARA analysis of the high-viscosity oil of the Ashalchinsk deposits and of the aquathermolysis products indicate that the nature of the metal in the oil-soluble catalyst has different effects on the composition of the heavy oil. It is known that the presence of steam in the reaction medium at temperatures in the order of 300°C even without the catalyst leads to destruction of the carbon–heteroatom bond of the resin–asphaltene components. In a control experiment representing the aquathermolysis process without the use of catalytic agents the asphaltenes increase by almost 1% with increase of the fraction of saturated hydrocarbons and with small decrease of the resins. This can be explained by initiated polymerization in the experiment as a result of open radical sites formed during cleavage of the least stable bonds of the high-molecular-weight resins and asphaltenes and removal of the alkyl side chains. The introduction of the catalyst precursor into the aquathermolysis process reduces the proportion of the high-molecular-weight fractions in the composition of heavy oil considerably (by more than 10%). The asphaltene content in the case of the use of the catalyst based on iron is reduced by 1.4% compared with aquathermolysis without the catalyst. The proportion of resins decreases considerably from 25.18 to 18.32% for the catalyst based on iron and 18.45% for the catalyst based on cobalt. A considerable increase in the proportion of saturated hydrocarbons is observed in all the products of catalytic aquathermolysis.

The changes in the group composition of the heavy oil are reflected in the change of its viscosity–temperature characteristics (Fig. 1). Investigation of the catalytic activity of the carboxylates of the metals iron and cobalt in an inert atmosphere showed that the viscosity of heavy oil can decrease by approximately 50% at 10°C.

During the hydrothermal–catalytic processes the high-molecular-weight components of the oil undergo changes associated with destruction of the high-molecular-weight structures mostly at the sulfur-containing bonds, as demonstrated by the decrease of the total sulfur content in the asphaltene fraction of the products (Table 2). Decrease of the ratio of hydrogen to carbon can also indicate destruction of the least stable hetero-containing compounds, as a result of which the heavy components dissociate into fine particles with removal of the alkyl chains, leading to decrease of the viscosity of the heavy oil.

The isolated powder of the active form of the catalyst was identified by x-ray diffraction analysis, and the size of the catalyst particles was estimated by scanning electron microscopy.

The transformed copper and cobalt tallates are mostly represented by sulfide compounds (Fig. 2) whereas the iron tallate is transformed preferentially during aquathermolysis into the oxide form. It is seen from the results of x-ray structural analysis that the samples of the transformed precursors based on the metals cobalt and iron consist predominantly of one type of compounds of the metals. Thus, the catalyst based on cobalt is represented by the sulfide compound Co_9S_8 , which is also confirmed visually by its yellow color and metallic lustre. The powder of the precursor based on iron consists mainly of Fe_{29}O_4 (75%), which is confirmed by its magnetic properties. The formation of the sulfide compounds is evidently favored by cleavage of the C–S bonds in the structure of the resins and asphaltenes, which subsequently leads to interaction with the metal ion during decomposition of the catalyst precursor. The formation of magnetite probably arises from the presence of oxygen both in the heteroatomic compounds of the oil itself and as a result of the decomposition of water.

Photographs of the catalysts obtained by scanning electron microscopy are presented in Fig. 3. It can be stated that the obtained powders of the catalysts are nanosized particles of compounds of the metals. The particle sizes of all the samples vary in the range from 50 to 70 nm.

The investigations have demonstrated the effectiveness of using the catalysts based on transition metals formed from oil-soluble precursors to intensify the transformation of heavy oil in the aquathermolysis

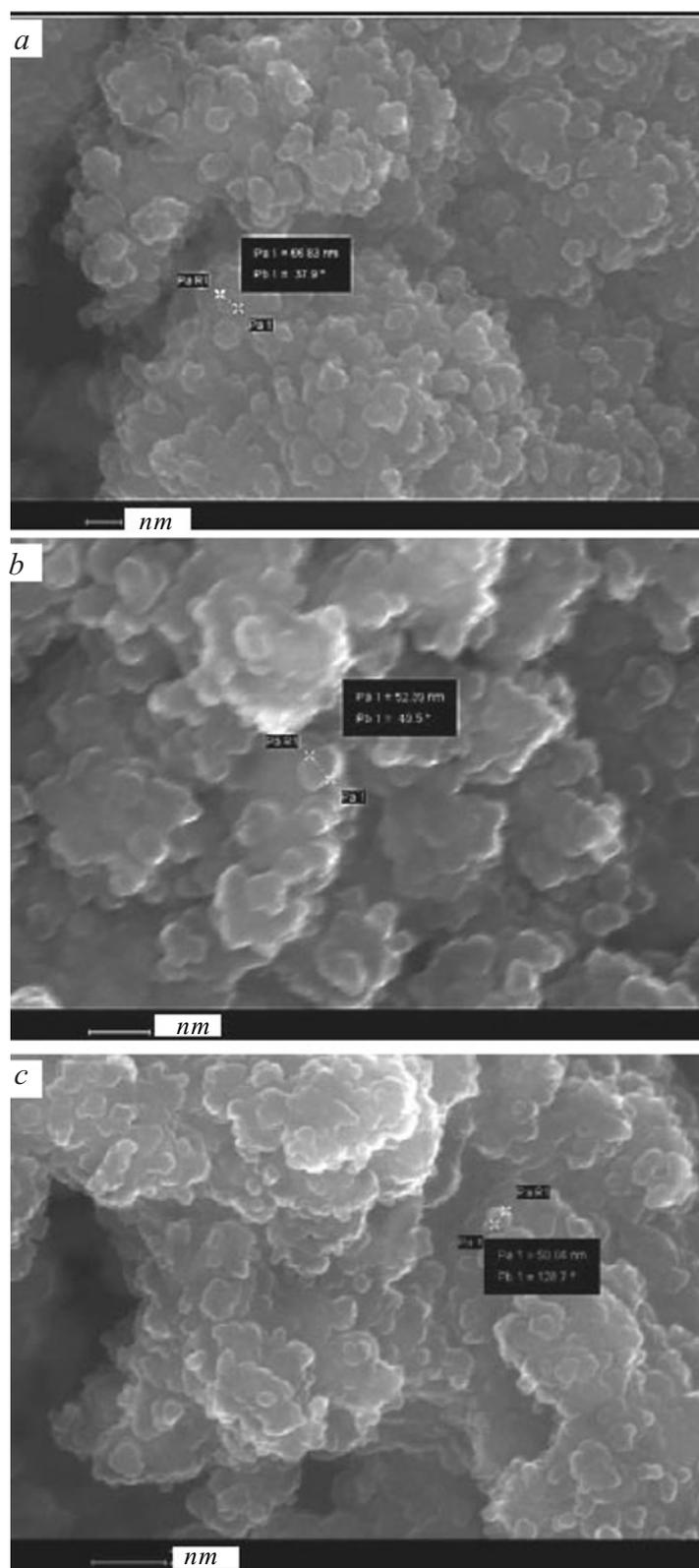


Fig. 3. Photomicrographs of the isolated particles of catalysts based on cobalt (a), iron (b), and copper (c).

process. The results from analysis of the group composition indicate significant lowering of the high-molecular-weight structures of the oil on account of thermocatalytic degradation. This produced a decrease in the viscosity of the heavy oil. The active form of the catalyst is in the form of nanosized particles of the metal compound. According to the results from SEM the particle size of the catalysts lies within a range of 60 nm.

The data from x-ray structure analysis show that the oil-soluble precursor of the catalyst based on cobalt is transformed during aquathermolysis into the sulfide form of the metal while the catalyst based on iron is transformed into the oxide form of the metal. Catalysts of such types are used in hydrocracking and hydrofining of oil fractions. By using catalysts based on metals of the transition groups in steam-heat extraction metals it is therefore possible to increase the degree of desulfurization, to reduce the viscosity of the heavy oil, and to raise the degree of oil extraction.

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