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Composition of aquathermolysis catalysts forming in situ from oil-soluble catalyst precursor mixtures

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ABSTRACT

Increasing efficiency of thermal recovery methods of heavy oil through injection of destructive hydrogenation catalysts precursors is a relevant task. In this paper the composition and properties of the active binary catalysts, which formed from a mixture of oil-soluble iron-, nickel- and copper-based precursors have been studied by XRD, Mössbauer spectroscopy, SEM, EDX-mapping methods. Moreover, the efficiency of a mixture of the corresponding metals in reducing the content of heavy components (SARA) of heavy crude oil from Ashal'cha field (Republic of Tatarstan) have been investigated. Mössbauer spectroscopy and EDX-mapping detected the formation of not only spinel ferrites MFe_2O_4 (where M = Ni or Cu), but also individual oxides. Moreover, in case of nickel-based catalyst three phases are formed: magnetite $FeO{\cdot}Fe_2O_3$, spinel ferrite $NiFe_2O_4$ and superparamagnetic finely dispersed phase of iron oxides (and probably nickel oxides). According to XRD results, the oxides formed in the first stage transform into nonstoichiometric spinel ferrites $Cu_{0.86}Fe_{2.14}O_4$ and $Ni_{1.43}Fe_{1.7}O_4$ under hydrothermal influences. It is related with the thermodynamically beneficial processes of conversion of this specific phase composition. Based on the SARA and elemental analysis of the initial and converted oil, it was found that catalytic aquathermolysis decreases the content of asphaltenes and resins (about 45%) in the presence of catalyst nanoparticles, which indicates an improvement in the quality of the heavy oil.

1. Introduction

The global demand of society for the energy is rising every day. At the same time, the structure of oil reserves changes as well. The heavy hydrocarbon resources represent a significant share of the total oil world reserves. This explains a magnificent interest and concentration of petroleum industry on unconventional and hard-to-recover hydrocarbons, particularly on heavy oils. The main restriction in their recovery is an abnormally high viscosity due to tremendous amount of resins and asphaltenes in heavy crude oil composition. However, there is a vast amount of researches focused on developing heavy oil recovery. Injection of various heat carriers into the reservoirs decreases the viscosity of heavy oil in situ and hence, provides their production. In case of steam injection, the temperature of carrier may attain 350–400°C, while the reservoir may be heated up to 200–250°C and higher. Obviously, in such temperatures, the chemical conversion of heavy oil components is possible. (Katritzky et al., 1990; Savel'ev et al., 2007; Gafurov et al., 2018).

The conduction of chemical conversions during steam treatment processes of heavy oil is justified by gas evolvement. Ruzin and Ursegov (2005) observed the hydrogen sulfide content in the products of oil from Usinskoe reservoir, developing by steam injection methods. The interesting results have been obtained while studying the influences of water phase condition on CO_2 yield. The catalytic activity of water steam, which increased the CO_2 yield by four times in contrast with a water in liquid state, was observed.

Thus, aquathermolysis is an in situ upgrading technique of high viscous heavy hydrocarbons. The aquathermolysis has a common principle with internal combustion, low temperature oxidation and other methods – injection of various reagents into the heated reservoirs (Weissman and Kessler, 1996). Yet, heavy crude oil cools down after the production in downstream conditions and the viscosity rises again. Consequently, the refinery of such crude oil becomes difficult due to the high content of resins and asphaltenes. It is generally accepted that steam treatment influences chemical conversion of asphaltenes. Many studies have been focusing on introducing catalysts for in-situ destructive hydrogenation of resins and asphaltenes (Muraza and Galadima, 2015; Petrov et al., 2017; Kayukova et al., 2018). The

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catalysts decrease the molecular mass of asphaltenes, as well as their content (Feoktistov et al., 2018; Vakhin et al., 2017; Kayukova et al., 2017; Salih et al., 2018).

Particularly, the catalysts intensify mainly the cleavage of the least stable C-S-C bonds, as well as the C-C bonds with the opening of the naphthalene ring, caused by the reactions of hydrogenolysis, cracking or oxidation (Kondoh et al., 2016; Kadiev et al., 2015; Alaei et al., 2017). Moreover, disjoining of peripheral fragments from high-molecular components of oil (resins and asphaltenes) and formation of hydrocarbons, heteroatom compounds, benzene resins occurs, which leads to changes in elemental, group and fractional compositions of heavy oils. Hence, the desulfurization degree rises and the viscosity of heavy oil decreases.

It is obvious that providing catalysts into the reservoir formations in the form of dispersed powder is impossible. The catalyst nanoparticles would be adsorbed by the walls of injection wellbores, not reaching even the drainage zone. Therefore, many researchers are working on the synthesis of catalysts for in-situ applications and their effectiveness in the aspect of enhanced oil recovery. As a method of investigation the physical simulation in the closed systems and flooding setups, as well as field tests are applied. (Tumanyan et al., 2015; Varfolomeev et al., 2016). Mainly, the catalysts are introduced in the nanoscale or an oil-soluble precursor form. The in-situ decomposition of precursors generates the active form of catalysts (Maity et al., 2010). The active form is essentially the oxides or sulfides of the corresponding metals (Vakhin et al., 2015; Ivanova et al., 2017; Galukhin et al., 2015).

Many researches are aimed to study the effectiveness of such catalysts in the form of precursors based on the individual metals, like e.g. iron, nickel, and copper. However, every metal in its active form influences the particular oil fractions. The effect of Co-based catalyst, introduced in the form of oil-soluble precursor, on reduction of resins (38%) and asphaltenes (26%) at aquathermolysis temperature of 180°C was revealed (Sitnov et al., 2016). Another example is a nickel tallate at 250°C influences the destruction of mainly resins (Kudryashov et al., 2017). Besides, the nickel provides decrease in sulfur dioxide content and increase in the content of carbon dioxide gas and water (Isakov et al., 2015). However, the cost of a cobalt-based catalyst is almost four times that of a nickel-based one.

Several scientists suggest to use the bi-, tri-metallic catalysts, which would form in situ from bi-, tri-metallic or monometallic precursor mixtures. However, it is shown in (Panariti et al., 2000) that the use of organic precursors containing two metals (Mo and Ni or Co) in the molecule has a negligible effect on the degree of desulfurization. This is not due to the formation of non-mixed sulfides but two phases: MoS_2 and the second metal sulfide. As it is known, transition metal sulfides catalyze the reaction of water gas. The reaction liberates hydrogen, which contributes to the processes of hydrocracking and hydrogenolysis (Jia et al., 2012). In addition to sulfides, a metal oxides and their spinels are formed (Vozniuk et al., 2017). For this reason, there is a deep interest to study the efficiency of a precursor mixtures based on various metals, as well as to study the composition of the active form generated in situ as a result of steam influences.

It is relevant to optimize the efficiency and reduce the cost of such catalysts by using a combination of different transition metals. This work has examined the composition and properties of the active shape of the catalyst provided in the reservoir conditions from a mixture of oil-soluble compounds of iron, nickel and copper. At the same time, an analysis was made for the efficiency of a mixture of the corresponding metals in the aspect of improvement of quality of heavy oil.

2. Materials and methods

2.1. Samples and modeling of the aquathermolysis

The object of this study was catalyst nanoparticles, formed from the precursors (mechanical mixtures of iron tallate with tallates of metals: nickel, copper in a mass ratio of 1:1) during aquathermolysis of the heavy crude oil from the Ashal'cha field of the Republic of Tatarstan. The catalysts were extracted from the oil after the aquathermolysis process. All precursors were derived from distilled tall oil (DTO) and the corresponding metal sulfate. DTO is a product of vacuum rectification of crude tall oil. DTO contains no more than 30% of resin acids, up to 6% of non-saponified substances and the rest are fatty acids (olein, linoleic, linolenic). Acid number ranges within 170–190 mg/g. In order to get enough amount of catalysts for their detail investigation, the share of precursors introduced to the oil was 40 wt %.

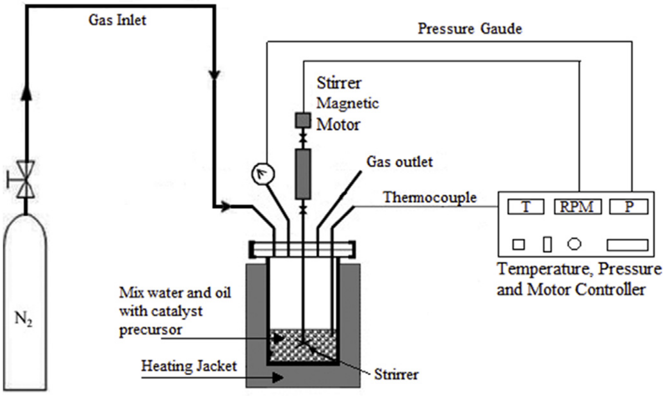

Fig. 1. Schematic representation of batch reactor for aquathermolysis.

The schematic representation of batch reactor for aquathermolysis is provided in Fig. 1. In batch reactor the certain amount of oil, catalyst precursor and water were put and the inert gas-nitrogen was injected from the top of the reactor for 10 min in order to remove oxygen. Then the specific temperature (250 °C) was adjusted from the controller. After the given temperature had stabilized, the average pressure in the reactor for all the experiments was 3.8 MPa. The treatment time was 4 h from the moment of the stabilized temperature. To observe the efficiency of catalysts, the given simulation conditions were kept except the treatment time, which was 6 h. The precursor was introduced in a solution of [H] - donor. In the oil bulk, the constant amount of catalyst precursors was 2.2 wt %, whereas the [H] - donor and water content were 2 wt % and 30 wt %, respectively. The solvent composed of aliphatic mixture, alicyclic and aromatic hydrocarbons (solvent naphta), is used as a [H] – donor (Tumanyan et al., 2015). The presence of compounds that can be the source of hydrogen (mainly cycloalkanes) were justified by GC-MS (Fig. 2) and see Table 1.

2.2. Methods

The catalyst nanoparticles were investigated by X-ray diffraction, Mössbauer spectroscopy, SEM and Energy-dispersive X-ray spectrum (EDX mapping) methods.

The X-ray diffraction analysis was accomplished using Shimadzu XRD-7000S automatic powder diffractometer using a nickel monochromator with a step of 0.008 nm and 3 s point exposure, in combination with a Bruker D2 PHaser and CuKα radiation with a wavelength of λ = 1.54060 nm.

Mössbauer spectra were acquired using a MS1104EM №40-12 spectrometer, which is made by the Research Institute of Physics, Southern Federal University, in the constant acceleration regime at room temperature. A scintillation counter with a thin (0.1 mm) NaI (Tl) crystal was used as a detector. The spectrum was obtained using a ^{57}Co (Rh) source. The velocity scale was calibrated according to α-Fe spectrum. Isomer shifts were measured from the centre of the spectrum of this standard absorber at room temperature. Mathematical processing